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# SYSTEMATIC QUALITATIVE ORGANIC ANALYSIS

BY

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# PREFACE

This book is intended mainly for the training of students in the general methods employed in the identification of organic compounds.

During the preparation of the book the author personally examined over 600 purely organic substances and a large number of their metallic derivatives. Conditions, necessary for a definite result, were found for every test, and then systematic schemes of analysis were built up. The solid derivatives, to be prepared for identification purposes, have been carefully selected. Where alternatives were possible, those with very low or very high melting points have been avoided. The author has prepared all the derivatives mentioned and determined their melting points. This work has been carried out in order that detailed methods of preparation, either general or special, could be given; also in a considerable number of cases for the purpose of deciding between the widely different values for the melting point of a particular compound given in works of reference. For purposes of economy, derivatives for whose preparation only relatively inexpensive reagents are required, have been chosen.

By following out the schemes and the instructions for the preparation of derivatives students obtain decisive results, and thus gain confidence in their work.

Particular attention has been paid to the requirements of pharmaceutical students, the schemes permitting of the rapid identification of the majority of the single organic compounds included in the British Pharmacopœia.

The time factor has always been kept in mind, the minimum times for the various treatments having been found. The times required for the hydrolysis, under the specified conditions, of about 100 esters are given. Thus if an ester is required to be hydrolysed in an examination, or during a brief practical period, one which is suitable may be chosen from the lists.

For students taking lecture courses, but not requiring analytical work, the book provides rapid exercises in the processes employed in practical organic work. Using the small quantities of substances indicated, even part-time day or evening students can gain considerable practical experience in a short time, and with but little expense to the institution they are attending. A special index of such exercises, not involving analysis, is included.

Certain classes of compounds have been omitted, as it is considered unlikely that students will encounter them; also the identification of dyes and their more complex intermediates is considered beyond the scope of the work.

The author has aimed at producing an essentially practical book, hence chemical equations and explanations have been omitted. Students of Organic Chemistry will usually be attending lecture courses, where equations will be given and reactions explained. In the case of the simpler compounds given for identification it is suggested that, after the completion of their practical work, students should give an account of the reactions involved, gaining the required information from lecture notes, text-books, or other sources. Knowledge gained in this way will be far more interesting, and will be retained for a longer period, than if acquired without effort.

As but few names are mentioned, a general acknowledgment is here made to all chemists whose work has been utilised.

The author is greatly indebted to his colleague, Mr. M. Greenwood, M.A. (Oxon.), for his careful and helpful criticism of the text.

H. MIDDLETON.

The Senior Chemical Laboratory,
Bradford Technical College,
*December* 1938.

## PREFACE TO THE SECOND EDITION

Some of the schemes for the determination of the class of a compound have been rewritten so that by applying *all* the tests in the scheme considerable information concerning the presence of groups in an organic compound, not listed in the book, may be gained.

About thirty more compounds, mainly aldehydes and ketones, have been added to the lists of substances.

H. M

*September* 1943.

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## STANDARD ABBREVIATIONS

| | |
|---|---|
| aq. (before a formula usually indicates the ordinary laboratory reagent) | aqueous |
| b.p. | boiling point |
| conc. | concentrated |
| c.c. | cubic centimetres |
| *d.* (always followed by a number) | density |
| dil. (before the formula of a mineral acid indicates an approximately twice normal solution) | dilute |
| equiv. | equivalent |
| g. | gram(s) |
| m.p. | melting point |
| N. (in connection with standard solutions) | normal |
| *n.* (in connection with isomers) | |
| ppt. | precipitate |
| *sec.* | secondary |
| soln. | solution |
| *tert.* | tertiary |
| t.t. | test-tube |
| vol. | volume |
| wt. | weight |
| decomp. (in connection with m.p.) | with decomposition |
| Me | Methyl, $CH_3$— |
| Et | Ethyl, $C_2H_5$— |
| Ph | Phenyl $C_6H_5$— |
| Ac | Acetyl, $CH_3{\cdot}CO$— |
| Bz | Benzoyl, $C_6H_5{\cdot}CO$— |
| R | Radical (alkyl or aryl) |

## SPECIAL ABBREVIATIONS

| | |
|---|---|
| O.S. | Original substance |
| R.G. | Rice grain |

# SYSTEMATIC QUALITATIVE ORGANIC ANALYSIS

## INTRODUCTION[1]

Organic substances are carbon compounds.

The presence of carbon in a substance is indicated by one or more of the following results:

(1) The liberation of carbon, which may be left as a black residue when the substance is heated on platinum or porcelain, or in the case of inflammable substances deposited as soot when a cool surface is held in contact with the flame of the burning substance.

In either case the black substance is proved to be carbon by the fact that on heating to redness it burns away completely.

(2) The production of a characteristic blue flame, due to the burning of carbon monoxide, when the substance is warmed in a test-tube with concentrated sulphuric acid and the mouth of the tube turned to the flame.

(3) The milkiness produced in limewater by passing through it the carbon dioxide evolved when

(*a*) a dilute mineral acid is added to the substance.

This applies to most carbonates, those containing a metal being usually regarded as inorganic substances.

(*b*) a mixture of the substance and finely divided copper oxide is heated to redness, or the vapour of the substance is passed over red-hot copper oxide in a suitable apparatus.

For the identification of a single carbon compound it is generally advisable first to test for the elements present.

It is assumed that the substance under examination will contain carbon and one or more of the following elements: hydrogen, oxygen, nitrogen, sulphur, chlorine, bromine, iodine, phosphorus, arsenic, common metals.

The test for hydrogen, which depends on the formation of water (detected by the blue colour given to anhydrous copper sulphate) when the substance is heated with copper oxide is not worth while, owing to the time involved in the complete drying of the substance and the copper oxide. The few common organic substances which, if anhydrous, contain no hydrogen (e.g. carbon tetrachloride, hexachloroethane, metallic oxalates, etc.) present no difficulty in detection.

---

[1] Before commencing work this introduction should be carefully read.

The presence of oxygen is usually inferred by the recognition, during the identification, of a characteristic group e.g. —OH. The next procedure is usually the determination of the class of the compound, i.e. to ascertain whether it is an alcohol, carbohydrate, amine, etc.

Finally the compound is identified as a particular member of a class by some or all of the following methods:

(*a*) comparison of the physical properties of the substance with those of known members of the class.

(*b*) application of special chemical tests.

(*c*) preparation from the compound, if possible, of a pure solid substance known as a "derivative," and determination of its melting point. Reference is then made to a list of melting points of the particular derivatives in order to ascertain if the melting point obtained is identical with, or near to, that of one of the derivatives in the list.

(*d*) quantitative work, e.g. determination of the equivalent weight of an acid, or estimation of the percentage weight of a particular group present.

## *EXPERIMENTAL TECHNIQUE*

The substance to be identified will be referred to throughout the book by the letters O.S. (= original substance).

### (1) Measurement of quantities, etc.

In all the tests given the quantities which produce suitable results have been found by trial, hence to ensure equally definite results quantities approximately equal to those mentioned should be used (the word "approximately" should not be interpreted too liberally). For either a solid or a liquid a certain depth (referred to for convenience as a "layer") in a test-tube of the width usually employed (⅝ in. diameter) is mentioned, the depth referring to the vertical distance between the surface of the substance and the lowest part of the curved bottom of the tube.

Except when the word "measured" precedes the figure, the measurements are intended to be made roughly with the eye, but it might be advisable at the beginning to glance at a rule.

It should be noted how much of a solid substance it is necessary to take up on the end of a spatula to approximate to a $\frac{1}{8}$-in. layer in the test-tube mentioned, since it is not to be expected that a dry tube will be used every time and if the tube is wet most of the substance will stick to the sides and all idea of measurement by means of the tube will be lost.

Unless a solid substance is in the form of a reasonably dense powder it should be ground up in a mortar.

In the case of solids the letters R.G. are used to indicate an amount roughly equal in bulk to a large rice grain.

By a " trace " is meant an amount roughly equal in bulk to an ordinary pin-head.

Volumes of liquids are also referred to in c.c.

A 5-in. × $\frac{5}{8}$-in. test-tube has a capacity of approximately 20 c.c., hence if this length of tube is employed 5 c.c. will refer to a quarter of a test-tube full, and so on. For 1 c.c., 2 c.c., and 3 c.c. it will be sufficient to employ respectively a depth of $\frac{1}{4}$ in., $\frac{1}{2}$ in., and $\frac{3}{4}$ in.

In the tests definite volumes are stated, but they are only intended to be approximate unless in italic type; the same applies to the times given in the directions.

### (2) Use of litmus paper.

Experience has shown that often correct results are not obtained because the volume of acid or alkali added for the purpose of acidifying, or rendering alkaline, a solution is inadequate. Hence when it is necessary to render a solution acid or alkaline, the acid or alkali should be added whilst stirring with a glass rod until a drop of the solution removed on the end of the rod gives the required reaction with litmus paper. The method of preparing a perfectly neutral solution is given elsewhere.

### Procedure for the identification of O.S.

(1) Determine the elements present by applying Tests 1–7 (pages 5–10). If only negative results are obtained assume O.S. contains C and H, and possibly O. Also apply Test 8, if applicable.

(2) Ascertain the class of O.S. by means of an appropriate scheme (see page 11), then follow the instructions given in order to identify O.S. as a particular member of the class.

### Notes concerning the class schemes and sections.

(1) If a test depends on the production of a certain odour with which the student is not familiar, he should obtain some of the substance mentioned and compare its odour with that produced in the test.

(2) Methods for the determination of m.p. and b.p. are described on pages 12–15. A reflux apparatus is illustrated on page 17 (Fig. 5), and a distillation apparatus on page 22 (Fig. 11).

(3) It is probable that the majority of substances given for

identification will not require purification before analysis. Dark coloured liquids (e.g. bases, furfural, etc., which become brown with age), however, may be encountered, and in order that clean derivatives may be prepared such liquids should be redistilled in the manner described under " Method 1 " (page 14). Also if the appearance of a solid substance indicates that it is impure (or the m.p. is found to be indefinite) recrystallisation should be carried out in the manner described under " Choice of a solvent " (page 19).

(4) In cases where a substance, whose class has been ascertained, cannot be identified as one of the compounds listed in the class section, or if further information concerning a particular compound is desired, reference should be made to comprehensive works such as the following :

Heilbron, *Dictionary of Organic Compounds.*
Mulliken, *Identification of Pure Organic Compounds.*
Beilstein, Prager, Jacobsen, *Organische Chemie.*

# TESTS FOR ELEMENTS

Ignition tubes required for some of the tests may be prepared as follows:

Heat in a Bunsen flame with continued rotation, the centre of a piece of soft thin-walled glass tubing, ¼-in. outside diameter and 5 in. long. When the glass is soft enough remove the tube from the flame and draw out to a total length of 12 in.–14 in.; allow to cool. Cut with a file in such a way that two wide tubes are obtained, having at one end a tapering portion about ¼ in. long. Rotate the tapered end in the flame until sealed and continue heating and rotating until there is at the end of the tube a rounded, red-hot mass of glass about ⅛ in. deep. Remove from the flame and blow down the tube until a bulb slightly wider than the tube is formed. Cut that portion of the capillary tube, which is of more or less uniform bore, into 2-in. lengths and retain these for use in melting point determinations.

**(1) Beilstein's test for halogens.**

Insert one end of about 4 in. of stout copper wire into a cork and bend about ½ in. of the other end over so that it lies practically parallel to the longer length of the wire. Heat the bent end of the wire until it ceases to impart any colour to the flame, then allow it to cool. Place a little O.S. on a clean watch-glass and dip the wire into it; in the case of a solid a little pile should be on the end of the wire. Heat the end of the wire in the lower outer edge of the flame and wait until any yellow colour, due to the burning of the substance, has disappeared.

No green colour indicates the absence of halogen (see note).

A green colour is produced if halogen is present, but the same colour is given by several substances which contain no halogen, hence Test 4 must be applied in order to ascertain if halogen is really present, and if so, whether it is Cl, Br, or I.

NOTE.

The green colour may be masked by a yellow sodium flame.

(2) ***If O.S. is a liquid,*** to ¼-in. layer of it in a t.t. add 3 c.c. distilled water and shake. Test the mixture with red litmus paper.

An alkaline reaction indicates that O.S. contains N.

If O.S. has not mixed with the water, add a drop of iodine solution, shake, and allow to stand until the layers separate.

A violet-coloured solution of iodine in O.S. indicates the absence of O in the latter; if the colour of the solution is red or brown, O.S. may, or may not, contain O.

### (3) Soda-lime test for N and Hg. (See notes.)

***If O.S. is***

***(a) a solid,*** grind an amount of freshly ignited soda-lime which would roughly fill the bulb of an ignition tube with about $\frac{1}{5}$ of its bulk of O.S. Place sufficient of the mixture in the tube just to fill the bulb. Heat the bulb by rotating it over a small flame and hold a piece of moistured red litmus paper about $\frac{1}{4}$ in. from the mouth of the tube.

If (i) the colour of the litmus paper is changed to a definite blue the presence of N in O.S. is indicated.

(ii) a grey sublimate is formed, rub it with the end of a match-stalk. The formation of metallic globules indicates that O.S. contains Hg.

***(b) a liquid,*** introduce into an ignition tube sufficient of it to half fill the bulb and add dry soda-lime to within about $\frac{1}{2}$ in. of the mouth of the tube. Heat the tube, beginning at the top of the soda-lime layer and slowly proceeding downwards towards the bulb.

Hold a piece of moistened red litmus paper about $\frac{1}{4}$ in. from the mouth of the tube. If the colour of the litmus paper is changed to a definite blue the presence of N in O.S. is indicated.

NOTES.

(i) The absence of alkaline vapours on heating O.S. with soda-lime does not indicate the absence of N in O.S.

(ii) ***If O.S. is a solid*** it should be noted if any odour (other than that of O.S. or ammonia) is evolved during the heating with soda-lime, as valuable information concerning the identity of O.S. may often be gained in this way.

Thus an odour of

(*a*) phenol or a cresol indicates that O.S. is a phenolic acid or a salt or ester of a phenolic acid. If O.S. contains S a sulphonic acid, salt, or ester is indicated.

(*b*) an amine indicates that O.S. is a salt of an amine, an acyl derivative of a primary or secondary amine, an amino-acid, or a salt or ester of an amino-acid. If O.S. contains S an aminosulphonic acid or salt is indicated.

The lower aliphatic amines possess ammoniacal, fishy odours; the odour of pyridine is peculiar and unpleasant; and the commoner aromatic amines possess odours similar to that of aniline or of dimethylaniline.

(*c*) bitter almonds indicates that O.S. is a derivative of benzaldehyde (bisulphite compound, oxime, etc.), a mononitrobenzoic acid, salt, or ester (nitrobenzene evolved) or an amide (e.g. benzamide which yields benzonitrile).

(*d*) benzene or toluene indicates that O.S. is a simple aromatic carboxylic acid, salt, or ester.

Whatever odour is detected the normal procedure for identification should be continued and tests shortened or omitted as far as the knowledge gained from the soda-lime test will permit.

(4) **Alkali-sugar test for S and halogens** and N in a limited number of cases. (Middleton, *The Analyst*, 1935, **60**, 154.)

***If O.S. is a solid,*** mix an amount equivalent to two or three times the bulk of a rice grain with about five times its bulk of alkali-sugar mixture.

Introduce the whole into an ignition tube and add alkali-sugar until, after tapping down, there is a column of the reagent about 1 in. long above the bulb.

***If O.S. is a liquid,*** introduce two or three drops into the bulb of an ignition tube and add alkali-sugar until, after tapping down, the column of reagent extends to within about ½ in. of the mouth of the tube.

Hold the tube horizontally (by means of tongs) and heat it in a flame about 2½ in. high, at first just beyond the column in order to prevent movement of the latter along the tube. Gradually extend the heating along the column, periodically turning the tube over to prevent undue bending. When a portion of the column equal in width to the flame is red-hot, hold the tube at an angle, so that while this portion still remains in the flame the heating is gradually extended until the bulb as well as the stem is in the flame. (It is essential that the whole column of reagent becomes red-hot before the organic substance in the bulb is heated.) Finally heat the whole tube to redness in a large flame for a minute or more, then plunge it into 10 c.c. of distilled water contained in a dish. (If necessary, break up the tube by tapping it with the tongs.) Heat the contents of the dish to boiling, continue boiling with stirring for ½ min., then filter. (If the filtrate is not colourless repeat the whole process, finally heating the whole tube more thoroughly.)

Apply the following tests to the alkaline filtrate:

(*a*) To 1 c.c. add one drop of aq. lead acetate.

A brown or black ppt. indicates that O.S. contains S. (Ignore a white ppt.)

(*b*) To 2 c.c. add two or three drops of aq. NaOH and one or two small crystals of $FeSO_4$, boil for ½ min., then cool. Just acidify with conc. HCl, heat to boiling and cool. (If S has been detected, add one or two drops of aq. $FeCl_3$ as the ferric salt formed by atmospheric oxidation may have been reduced by the $H_2S$ liberated.)

A blue ppt. or colour indicates that O.S. contains N. (A green soln., if filtered, may leave a blue residue.)

If a yellow or greenish yellow soln. is obtained apply Test 5 after Tests (*c*) and (*d*).

(*c*) To 2 c.c. add dil. $H_2SO_4$ until the soln. is just acid (if N or S is present, then dilute to 30 c.c. with water and boil down in a dish to 3–5 c.c.; cool), and add 1–2 drops of chlorine water.

If a yellow or brown soln. results, add about $\frac{1}{2}$ c.c. of chloroform and shake,

—chloroform coloured brown indicates that O.S. contains Br.
„ „ violet „ „ „ I.

If a violet chloroform layer is obtained, add Cl water drop by drop with shaking until the violet colour disappears.

If the chloroform now has a brown colour, this indicates that O.S. also contains Br.

(*d*) To the remainder of the filtrate add dil. $HNO_3$ until the soln. is acid (if N, S, Br, or I, is present, add to the acidified soln. an equal volume of dil. $HNO_3$, dilute to 30 c.c. with distilled water and boil down in a dish to 3–5 c.c.; cool), then add 1 c.c. aq. $AgNO_3$.

A white curdy ppt. indicates that O.S. contains Cl. (Ignore a faint milkiness.)

NOTE.

In the absence of sulphide, bromide and iodide, chloride may be detected in the presence of cyanide as follows: To the soln. (acidified with dil. $HNO_3$) add 1 c.c. aq. $AgNO_3$, then add aq. mercurous nitrate (5%) with shaking until the black coloration first formed has completely disappeared.

If a white ppt. remains, this indicates that O.S. contains Cl. (R. E. D. Clark, *J.C.S.*, 1936, 1050.)

(5) **Alkali-zinc test for N.** (Middleton, *The Analyst*, 1935 **60**, 154.)

(For advantages of this test see page 266.)

Follow the procedure described under (4) but using alkali-zin instead of alkali-sugar mixture.

To the alkaline filtrate apply only Test (*b*). The addition c $FeCl_3$ is not necessary as sulphide is never present in the alkalin filtrate.

(6) ***If O.S. is a solid,*** apply the following tests for the presence of a metal:

(*a*) **Borax bead test** as in Inorganic Analysis.

Compounds containing one of the metals which colour the borax bead are themselves usually coloured.

If no colour is given to the bead, apply Test (*b*).

(*b*) Place in a crucible sufficient O.S. to form a layer about ⅛ in. deep and moisten it with 50% $H_2SO_4$ (see note), using a dropping tube. Place the crucible on a pipe-clay triangle supported on a tripod *in a fume cupboard.* Heat until the contents of the crucible are dry, taking care that the mixture does not froth up too high. (If large bubbles form they should be broken with a glass rod.) Heat to redness, occasionally pressing down the residue, if bulky, with a glass rod until any carbon has burned away. (The oxidation of carbon is facilitated if, after the crucible has been allowed to cool, the contents are moistened with conc. $HNO_3$, heated carefully to dryness and finally to redness. In some cases no carbon will be liberated.)

An appreciable white or yellow residue of sulphate or oxide will be obtained if O.S. contains a metal. (Ignore any faint coloration or fine dust.)

**To identify the metal,** dissolve the residue if possible in water or dil. HCl, and proceed as in Inorganic Analysis. If the residue is insoluble in dil. HCl, ignite the organic substance by itself until fumes cease to be evolved and the residue is dry, then boil up with dil. $HNO_3$ and filter from any unburnt carbon.

NOTE.

50% $H_2SO_4$ refers to a mixture of equal volumes of conc. $H_2SO_4$ and water. At high temperature the acid has an oxidising action on carbon. Conc. $H_2SO_4$ is not suitable as it does not easily penetrate into the substance.

(7) **Oxidation test for P and As.**

In a nickel crucible (see note) supported on a pipe-clay triangle resting on a tripod place the equivalent of ⅛-in. layer in a t.t. of a mixture of equal weights of powdered $KNO_3$ and anhydrous $Na_2CO_3$. Heat until the solid has fused, remove the flame and add 2 R.G. of O.S. in minute quantities (each about equal in bulk to an ordinary pin-head), heating after each addition and waiting until all reaction has ceased before adding more. Finally heat until any carbon round the edges has burnt away completely. Cool the crucible, add 5 c.c. water and heat gently until the solid has dissolved. Pour the soln. into a t.t. and add conc. $HNO_3$

until the soln. is just acid. Pour 1 c.c. of the soln. into another t.t., add 3 c.c. ammonium molybdate soln., shake, and allow to stand for 2–3 min.

If (i) a yellow ppt. is formed, this indicates that O.S. contains P.

(ii) no yellow ppt. is obtained, heat to boiling and continue boiling for ½ min. or so.

A yellow ppt. indicates that O.S. contains As.

The following distinguishing test should also be applied: To the remainder of the acidified soln. add dil. $NH_4OH$ until it is just alkaline. Pour the soln. into a dish and boil until a piece of red litmus paper momentarily immersed in the soln. is just no longer turned blue, keeping the volume between 3 c.c. and 5 c.c. by the addition, if necessary, of water. Cool the soln., and add 1 c.c. aq. $AgNO_3$.

A pale yellow ppt. indicates P; a reddish ppt. indicates the presence in O.S. of As.

NOTE.

A porcelain crucible is not advisable owing to the possibility of calcium phosphate being one of the constituents of the porcelain.

**(8) Tests for halide, sulphate, and phosphate in solid compounds containing N.**

If in addition to N

(*a*) halogen has been detected, to ⅛-in. layer of O.S. in a t.t. add 5 c.c. distilled water, heat to boiling and if O.S. has not dissolved continue boiling for ½ min. Cool and if any solid is present, filter. To the soln. or filtrate add 2 c.c. dil. $HNO_3$, and then add 1 c.c. aq. $AgNO_3$. A white, pale yellow, or yellow ppt. indicates that O.S. is probably a halide salt of a base. (A similar result would be obtained with an acid halide of a N-containing carboxylic acid.)

(*b*) S has been detected, to ⅛-in. layer of O.S. in a t.t. add 5 c.c. dil. HCl, heat to boiling and if O.S. has not dissolved continue boiling for ½ min. Cool and if any solid is present filter. To the soln. or filtrate add 1 c.c. aq. $BaCl_2$. A white ppt. indicates that O.S. is the sulphate of a base.

(*c*) P has been detected, to 3 c.c. $NH_4$ molybdate soln. add R.G of O.S., shake and allow to stand for 1 min.

The formation of a yellow ppt. indicates that O.S. is the phosphate of a base.

## *INDEX OF CLASS SCHEMES*

In the second and succeeding schemes and in miscellaneous compounds only elements additional to those mentioned in Scheme I are indicated.

Page
*Scheme I* Compounds containing carbon and one or more of the following elements: H, O, metal . 25
*Scheme II* Compounds containing Cl, Br, or I . . 131
*Scheme III* Compounds containing S, or S and Cl . . 153
*Scheme IV* Compounds containing N, or N and halogen; also solid compounds containing N with sulphate or phosphate . . . . . . 165
*Scheme V* Compounds containing N and S (not as sulphate) . . . . . . . . 249

*Miscellaneous compounds:*

N, Cl, and S (not as sulphate)
P
As and N
As, N, and S
present . . . . . 258

NOTE.

In the heading on left-hand pages, those elements which may or may not be present in the substance under investigation are in brackets.

# *DETERMINATION OF PHYSICAL PROPERTIES*

## Determination of the melting point of a solid.

Fit up the apparatus shown in Fig. 1 and support the boiling-tube by means of a clamp and stand so that the bottom is about 8 in. above the bench. Into the boiling-tube pour a suitable liquid (see note 1) to the depth of about 1½ in.

Place on a watch-glass a little of the well-dried substance (see note 2) the m.p. of which is to be determined, and powder it finely by pressing and rubbing it with the end of a suitable spatula.

Gently stab the open end of a capillary tube (prepared in the manner described on page 5) several times on to a little heap of the powder, in order to introduce into the tube an amount of substance, which, after tapping the closed end of the tube on the bench each time, finally forms a tightly packed layer, $\frac{1}{16}$ in.–$\frac{1}{8}$ in. deep, at the bottom. (If the substance is waxy in nature a somewhat wider capillary tube may have to be used.)

Proceed similarly with a second capillary tube.

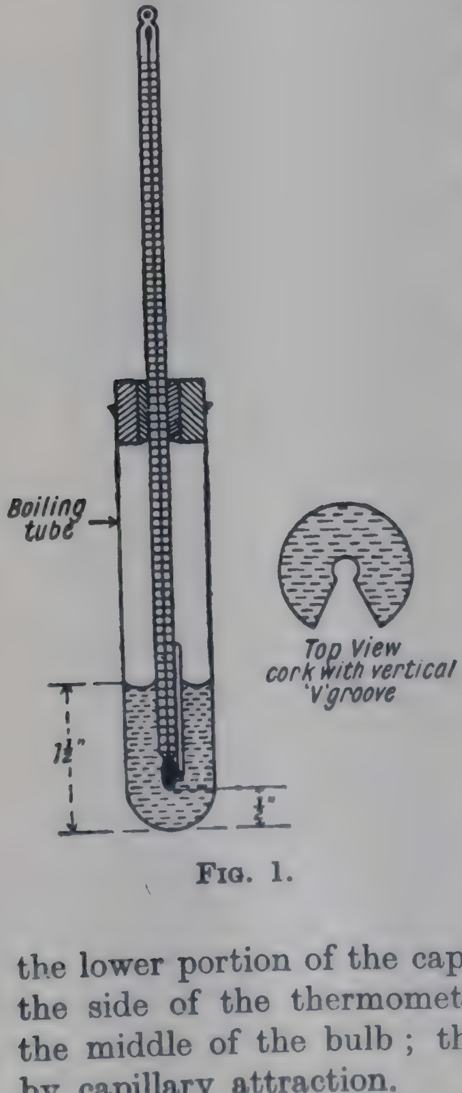


FIG. 1.

Remove from the boiling-tube the cork and thermometer, and stroke the moistened end of the latter along the lower portion of the capillary tube, then press the tube against the side of the thermometer so that the substance is opposite the middle of the bulb ; the tube will adhere to the thermometer by capillary attraction.

Replace the cork and thermometer, gently heat the liquid with a small flame, and note the temperature at which the solid changes to a transparent liquid (see note 3); an approximate value of the m.p. is thus obtained.

Carry out a more accurate determination at once, by repeating the procedure with the other capillary tube, raising, degree by degree, the temperature to which the liquid has fallen by periodically waving a small flame (about $\frac{3}{4}$ in. high) under the bottom of the boiling-tube until the m.p. of the solid is reached. With a little practice it is possible to reach, and not exceed or only slightly exceed, a particular temperature. (With this form of apparatus, where the liquid is not stirred, the flame should not be kept continuously under the boiling-tube, or the thermometer will register a temperature which is actually below that of the liquid.)

For each determination a freshly packed capillary tube should be used.

NOTES.

(1) For temperatures up to about 210° medicinal paraffin or glycerol are suitable and reasonably safe liquids to use.

For temperatures up to about 260° fresh concentrated sulphuric acid may be used, a crystal of $KNO_3$ being added to oxidise charred matter and prevent the acid from becoming discoloured. With this liquid, however, there is risk of serious injury should the tube break; safer liquids are esters of high b.p., e.g. butyl phthalate (b.p. 338°).

(2) It is essential that the substance be dry, since even a trace of moisture may lower the m.p. considerably.

For methods of drying substances see page 19.

(3) A pure compound usually has a sharp m.p., i.e. it melts completely within a range of about 1°. Any impurities present nearly always lower the m.p., and also render it indefinite, i.e. the change from solid to liquid extends over a number of degrees.

It may be necessary to recrystallise a substance one or more times before it melts sharply.

Some substances on heating undergo decomposition before the m.p. is reached, the decomposition products then acting as impurities and lowering the m.p. Even for these the method described (i.e. the introduction of the capillary tube into the liquid at a temperature only a little below the m.p. of the substance) enables a fairly accurate m.p. to be obtained, since the compound is exposed to the high temperature for only a short time before melting, and thus only slight decomposition occurs. If the substance and thermometer are placed in the cold liquid and the temperature raised slowly a much lower m.p. will be obtained.

(4) Since an ordinary thermometer may be inaccurate it should be standardised by using a range of pure substances of known m.p. (see note 2).

The following are suitable for the purpose: phenyl salicylate, m.p. 42°, naphthalene, m.p. 80°, benzoic acid, m.p. 121°, pyrogallol triacetate, m.p. 161°, quinol dibenzoate, m.p. 199°.

The m.p.s obtained in the manner described, and those usually given, are "uncorrected," i.e. no account has been taken of the fact that the mercury in the stem of the thermometer outside the liquid is not at the same temperature as that in the part of the thermometer immersed in the liquid.

**Identification by mixed melting points.**

If an unknown solid A, by reason of its m.p., is suspected to be a particular compound B, mix intimately about equal quantities of A and B, and determine the m.p. of the mixture.

If A is identical with B, the mixture will have the same m.p. as B; if, however, the two substances are not identical, the m.p. of the mixture will be considerably lower than that of either, and also indefinite.

**Determination of the boiling point of a liquid.**

If several c.c. of the specimen are available Method 1, which gives more accurate results, should be used; if, however, only 1 c.c. or less of liquid is available Method 2 should be employed.

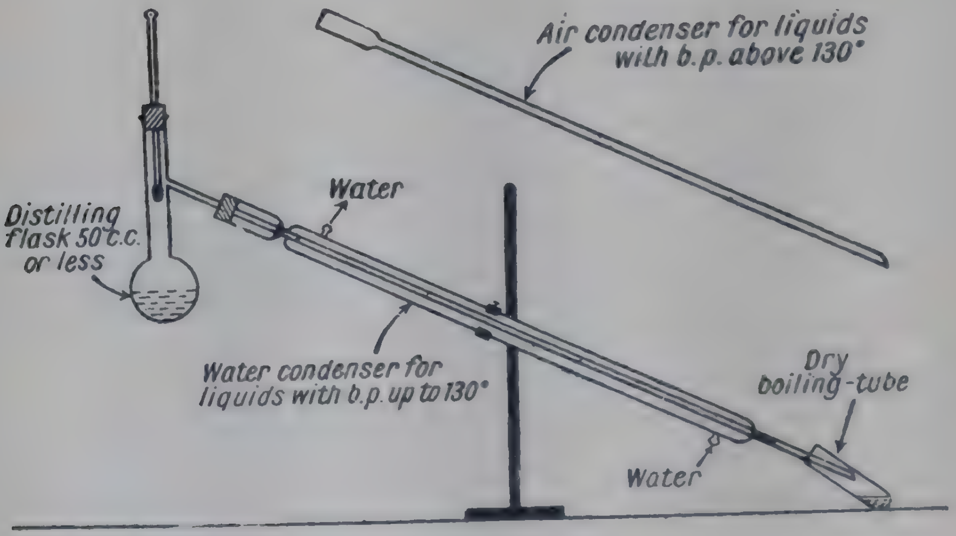

Air condenser for liquids with b.p. above 130°
Water
Distilling flask 50 c.c. or less
Water condenser for liquids with b.p. up to 130°
Dry boiling-tube
Water

Fig. 2.

*Method 1.* Fit up the apparatus shown in Fig. 2 and see that the top of the thermometer bulb is just level with the centre of the side tube of the flask. Disconnect the distilling flask from the condenser, remove the cork and thermometer, and pour in sufficient of the liquid to not more than half fill the bulb. Add two or three pieces of porous pot in order to facilitate regular boiling. Replace the cork and thermometer, taking care that, when fitted, the bulb of the latter is not touching the inside of the neck of the flask. Connect the flask to the condenser, and gently heat the liquid by means of a small flame in order to cause distillation at the rate of one or two drops a second.

If the liquid is pure, and is volatile without decomposition, practically the whole of it will pass over at a constant temperature, which is the boiling point of the liquid; when, however, only a small amount of liquid remains in the distilling flask the vapour may become superheated and a temperature rather higher than the correct b.p. may be registered.

If during the distillation the temperature continually rises, this is an indication that the liquid is not pure, or consists of a mixture of substances.

A constant b.p., however, does not necessarily indicate that the liquid possessing it is pure, as it may be due to a constant boiling mixture.

*Method 2.* Into a glass tube (about 2 in. long, and about ¼ in. diameter, sealed at one end) pour the liquid to a depth of about ¼ in. By means of a rubber band attach the tube to the thermometer of a m.p. apparatus (see page 12) so that the closed end of the tube is opposite the centre of the thermometer bulb. In the tube invert a capillary tube, about 2¼ in. long, and sealed at one end (i.e. such as is used for m.p. determinations) so that the open end rests on the bottom of the wide tube beneath the liquid. (Fig. 3.)

Replace the cork and thermometer with the attachment in the m.p. apparatus, and heat the liquid in the boiling-tube until a very rapid stream of bubbles issues from the open end of the capillary tube. Remove the flame, and note the temperature when the evolution of bubbles from the end of the capillary tube just ceases, this being the b.p. of the liquid.

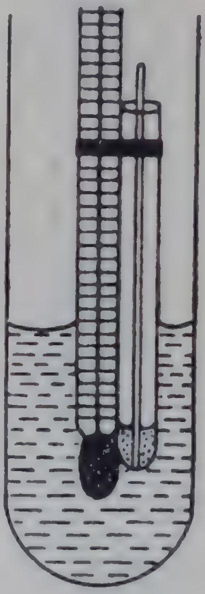


FIG. 3.

For each further determination use a fresh capillary tube.

B.p.s obtained by the above methods are as a rule a little lower than the standard b.p.s, partly because the whole of the mercury column of the thermometer is not usually in the vapour, and partly because such b.p.s are recorded at the existing atmospheric pressure which is generally less than the standard pressure of 760 mm.

**Filtration by suction.**

Solid precipitates or crystals should always be filtered off from the liquid present by suction, since not only is the method much more rapid than ordinary filtration, but it also permits of the almost complete removal of the liquid.

(In the method described an inexpensive, ordinary type of conical funnel is employed. If available, a small porcelain Büchner funnel, or a glass funnel with a plate of sintered glass, is more convenient.) Fit a filter flask (a thick-walled conical flask with a short side-tube for connection to a water pump) with a glass funnel (2 in.–$2\frac{1}{2}$ in. diameter) by means of a bored rubber stopper. (Fig. 4.) Place in the funnel a perforated porcelain disc. ($\frac{3}{4}$-in. diameter is a convenient size.) Cut a circle of filter paper (see note, page 16) about twice the diameter of the disc, and fit it roughly in the funnel over the disc. Moisten the paper with water (or the solvent used for crystallisation), then press it flat with the fingers on to the disc, and mould the edges against the sides of the funnel. Connect the filter flask to the water pump by means of pressure tubing, start the suction, and pour the mixture of solid and liquid gradually on to the middle of the filter paper. If a considerable amount of solid is present, press it well down on the filter paper by means of a spatula or cork, and maintain the suction for a minute or two in order to remove as much liquid as possible.

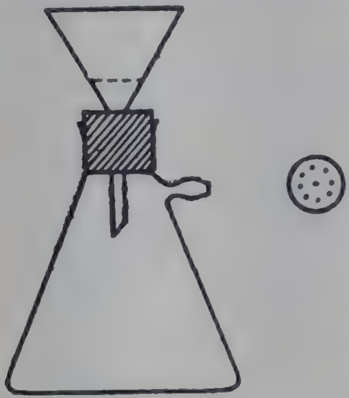


FIG. 4.—Filter Flask.

NOTE.

Smooth filter paper is preferable since the solid can easily be removed from it without being contaminated by paper fibre ; also it withstands the pressure better than the coarse variety.

**Washing of the filtered solid in the funnel.**

The filter flask should be disconnected from the pump whilst adding the liquid used for washing.

If the solid

(*a*) is crude, use the liquid suggested for this purpose in the instructions given for the preparation of the compound, in order to remove the reagents employed.

(*b*) has been crystallised, in order to remove mother liquor allow drops of the solvent, used for crystallisation, to fall over the whole surface. (If, on the addition of a drop of the solvent, the crystals are observed to dissolve readily, omit the washing.) In either case connect the flask again to the pump, and maintain the suction for several minutes in order to remove as much of the liquid as possible.

### Crystallisation of derivatives.

Transfer the derivative from the filter funnel to a dry boiling-tube or a dry 100-c.c. conical flask, or if the amount is small, to a dry t.t. Add sufficient of the recommended solvent just to cover the solid, and heat to boiling (see note 1).

If the solid does not dissolve completely, or almost completely (see note 2), gradually increase the amount of the solvent until, after heating again, solution of the solid is quite or almost complete.

If any solid is present, filter hot (see note 3). Allow to cool, or if speed is essential, cool by holding the tube or flask in a stream of cold water, meanwhile shaking. If crystals do not separate, scrape the glass in contact with the liquid with a glass rod; if still no crystals separate, evaporate off some of the solvent (see note 1), and cool again. If the derivative separates in the form of an oil whilst the soln. is warm, add a little more solvent, and heat again until a clear soln. is obtained, then allow to cool spontaneously, stirring and scraping with a glass rod from time to time. Filter off the crystals by suction and wash them in the manner described on page 16 (see note 4). Transfer the crystals to a watch-glass, and dry. (See "Drying of Substances," page 19.)

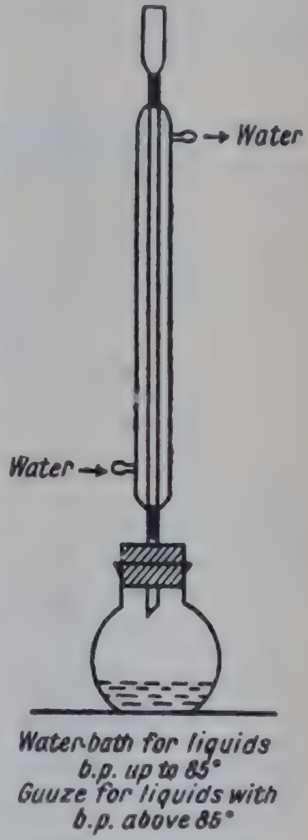

Water
Water
Water-bath for liquids b.p. up to 85°
Gauze for liquids with b.p. above 85°

Fig. 5.—Reflux Apparatus.

NOTES.

(1) Inflammable solvents, such as alcohol and acetone, should be heated (or evaporated down) by placing the tube or flask in water, which has been raised to a suitable temperature, and from which the source of heat has been removed.

In order to avoid loss of a readily volatile solvent, substances which dissolve slowly should be heated with the solvent in a flask fitted with a reflux condenser. (Fig. 5.)

(2) The solid may contain some impurity which is insoluble, or sparingly soluble, in the solvent employed.

(3) For the filtration of a hot soln., a fluted filter paper, and a

funnel, the stem of which has been cut off (Fig. 6), should be used; also the funnel should be warmed, and the soln. kept as hot as possible during filtration. First, however, it is advisable to cool the soln. slightly and if any solid is readily deposited, to add a little more solvent and reheat, in order to prevent the solid crystallising out in the filter paper; the excess of solvent may be removed by evaporation (see note 1) after filtration. When only a small amount of solid has been dissolved it is rarely that any other procedure will be necessary.

To prepare a fluted filter fold a filter paper into four, half-open it and double each quadrant inwards so that the edge is parallel to the centre crease A. Next double back each edge section, then fold each wide section backwards down the centre, finally fold down the middle crease so as to obtain a fan. Open out the filter and fold each of the two rectangular flutings down the centre.

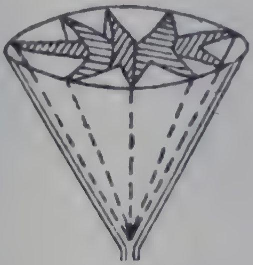


FIG. 6.

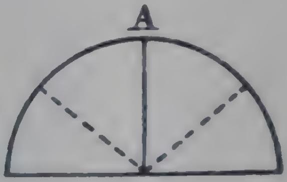


FIG. 7.

(4) For transferring the crystals from a tube or flask to the filter a glass rod, 6 in.–7 in. long, with a flattened end bent at a slight angle, will be found convenient. (Such a spatula may be made by heating the end of a glass rod until a red-hot round ball is formed, then pressing this between two charcoal blocks, and bending the flattened portion so that it forms a slight angle with the rod.)

If the quantity of crystals to be filtered is very small, a small, clean, dry filter flask should be used, a second filter flask being fitted between it and the pump in order to trap any water which may rush back through the pressure tubing if the pump for any reason ceases working. After filtration the mother liquor should be returned to the vessel which originally contained the mixture, and stirred or shaken to loosen crystals adhering to the sides of the vessel. The mixture should be again filtered, and the process repeated until all the solid has been transferred to the funnel.

### Crystallisation from mixed solvents.

*Use of aqueous alcohol* (*dilute alcohol*).

(1) For substances which are very soluble in cold alcohol and insoluble or sparingly soluble in water, a mixture of alcohol and water will often be a suitable solvent.

Either of the following methods may be adopted:

(*a*) Use a suitable mixture of alcohol and water in the manner described for a single solvent.

(*b*) Dissolve the substance in the minimum quantity of hot alcohol, and then add water drop by drop with shaking until a turbidity just appears. Heat until a clear soln. is just obtained, and allow to cool slowly. If only a small proportion of the dissolved solid crystallises out, reheat the mixture until a clear soln. is again obtained, add more water and repeat the above procedure.

If an emulsion appears during the cooling, dissolve it by adding a few drops of alcohol and stirring, thus keeping the soln. clear until the temperature is sufficiently low for crystallisation to start. Once crystals have separated the mixture may be cooled and stirred in order to complete the crystallisation rapidly.

(2) When a substance is moderately soluble in hot water, and readily soluble in cold alcohol, solution may be effected by boiling the solid with a volume of water insufficient for complete solution, allowing to cool somewhat, and then adding alcohol gradually with stirring or shaking until the remaining solid has dissolved. In this way a large volume of solvent is avoided.

*Glacial acetic acid and water*, or *acetone and alcohol* may be employed in the same manner as alcohol and water.

## Choice of a solvent.

If it is found necessary to recrystallise O.S., experiments must be carried out in order to find a suitable solvent. The commonest solvents are water, alcohol, aqueous alcohol, dilute acetic acid, acetone, a mixture of acetone and alcohol, benzene, petroleum ether. The procedure described under "Crystallisation of derivatives" (page 17) should be followed, using a ¼-in. layer of the powdered solid in a clean, dry t.t. A suitable solvent will be one of which 10 c.c. or less will dissolve the solid completely (or almost completely since insoluble impurities may be present) on heating, and which will permit of the separation of the bulk of the solid in crystalline form on cooling and, if necessary, scraping the glass in contact with the liquid with a glass rod.

## Drying of substances.

*Liquids.*

Proceed as with an ethereal soln (see page 22).

*Solids.*

If it is necessary to dry a small portion of a derivative as quickly as possible (e.g. for a m.p. determination), proceed as follows:

Place a thin layer of the substance on a piece of smooth filter paper, and move the paper slowly from side to side in a horizontal plane, 2 in.–3 in. above a small flame. If the substance shows signs of melting, increase the distance between the paper and the flame. Periodically move the substance about and turn it over with the blade of a penknife. Continue the procedure until the ease with which the substance can be shaken from the knife blade indicates that it is quite dry.

Fairly rapid drying may be achieved, whilst other work is being carried out, by standing the watch-glass containing the substance, on the bench at a suitable distance from a tripod on which a water bath, or a vessel on a gauze, is being heated by means of a Bunsen. If no vessel is being heated, a piece of asbestos board, or a gauze with an asbestos-covered centre, should be placed on a tripod so as to direct downwards the heat from a Bunsen placed beneath. A suitable position, i.e. one at which no melting, sublimation, or discoloration occurs, may be found by trial with a small quantity of the solid.

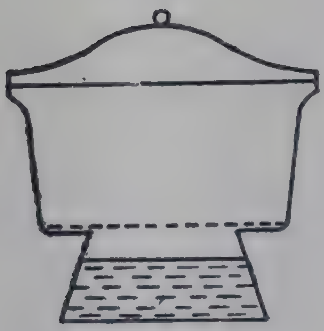


**Fig. 8.—Ordinary Desiccator.**

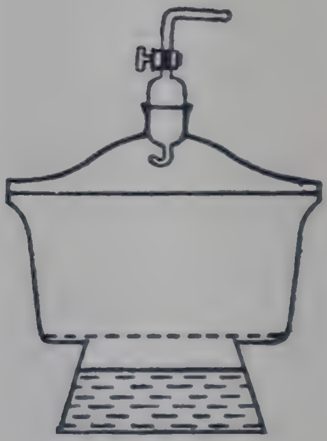


**Fig. 9.—Vacuum Desiccator.**

In some cases the substance may be safely and rapidly dried by placing the watch-glass on a charcoal block, standing lengthways or on end on the bench, as near to the flame as possible. Periodically during the heating the substance should be turned over and spread out with a spatula.

If speed is not essential, drying may be effected by placing the solid on a watch-glass in a desiccator (Fig. 8) containing some substance which will absorb the vapour of the solvent used for crystallisation or washing. Conc. $H_2SO_4$ is suitable for alkaline vapours, and the vapour of water or alcohol; solid NaOH is best for the drying of an amine hydrochloride, which has been crystallised from conc. HCl; whilst for the absorption of hydrocarbon vapours (e.g.

those of benzene or petroleum ether) freshly cut pieces of paraffin wax are suitable.

A vacuum desiccator (Fig. 9) is much more efficient than the ordinary type; when exhausting it by means of a water pump, a filter flask should always be fitted between the desiccator and the pump, in order to trap any water which may rush back through the pressure tubing when the pump for any reason ceases working. When opening the exhausted desiccator the air should be admitted slowly in order to avoid the dried substance being blown off the watch-glass.

## Extraction with ether.

*Procedure for the extraction of an oil from a mixture with water, or of a substance from its solution in water.*

CAUTION.

In all operations where ether is employed see that no flames are in the vicinity.

Cool the mixture or soln. to ordinary temperature, and pour it into a separating funnel (Fig. 10) (100 c.c. capacity will usually be suitable), then add to the mixture about ¼ of its volume of ether (see note 1). Insert the stopper, and hold it in place with a finger of the hand which is holding the funnel. Invert the funnel and release the pressure by opening the tap. Close the tap, shake for about a minute, inverting the funnel and releasing the pressure from time to time. Allow to stand until two well-defined layers are formed (see note 2). Remove the stopper, and run off the lower layer (which may be required) through the tap into a beaker. (The aqueous solution drawn off is always saturated with ether, and should not be heated over a free flame.) Replace the stopper, and move the funnel about so that the ethereal soln. flows all over the inner surface. Allow to stand, then run off any lower layer which has collected (see note 3). Pour the ethereal soln. through the neck of the funnel into a dry 100 c.c. wide-mouthed flask, and connect the latter to a water condenser. (Fig. 11.) Immerse the lower part of the flask in hot water contained in a beaker. Collect the distillate in a clean flask, and transfer it to a bottle for future use. (If the volume of the ethereal soln. is large, distil it in portions.) Remove the final trace of ether from the residue by heating the flask, without the cork, in boiling water for a few minutes, and blowing air (by means of bellows) over the residue.

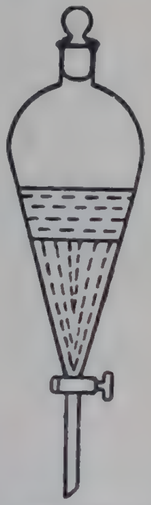


FIG. 10.—Separating Funnel.

NOTES.

(1) If a large quantity of solution is to be extracted, add some NaCl before the ether, since the latter is somewhat soluble in water but less so in brine; also many organic compounds are less soluble in brine than in water.

(2) If (*a*) the separation of the layers is very imperfect, add more ether.

(*b*) a stable emulsion is formed, add a few drops of alcohol, which will usually disperse it.

(*c*) solid is present in the lower layer, add water; if this does not dissolve it, filter the whole contents of the funnel, and pour the filtrate back into the washed-out funnel.

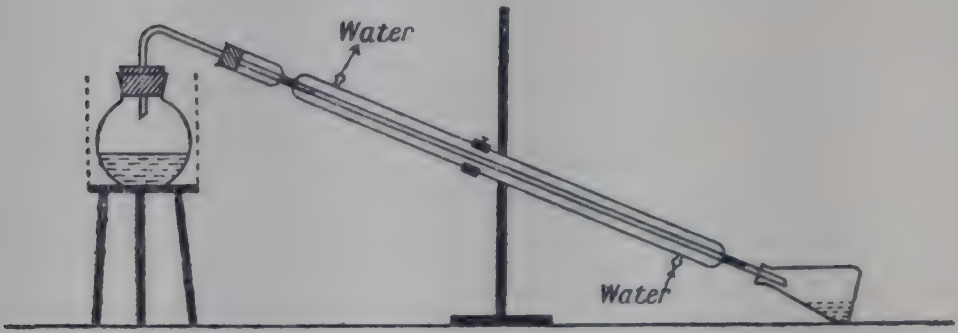


FIG. 11.—Distillation Apparatus.

For distillation of—

(*a*) Aqueous solutions: Heat the flask directly on a gauze.

(*b*) Ether or other very volatile liquids: Heat the flask by partially immersing it in hot water contained in a beaker, and see that no flames are in the vicinity.

(*d*) the substance to be extracted is in solution in water, extract several times with fresh quantities of ether, and add together the several extracts.

(3) *Washing and drying of the ethereal soln.*

If it is necessary to wash the ethereal soln. free from acid, alkali, etc., add about 3 c.c. of water for every 10 c.c. of ethereal soln., shake up, allow to stand, and run off the lower layer. Repeat this procedure until the wash water gives no test for the acid, etc., originally present. (The use of a large volume of water would soon greatly diminish the volume of the ethereal layer, since ether is somewhat soluble in water.)

When it is necessary to determine the b.p. or m.p. of the extracted compound, the ethereal soln. should be dried before distillation, since ether dissolves a little water. The drying agent to be used will depend on the nature of the compound dissolved in the ether.

For most substances fused $CaCl_2$ may be used; this substance, however, forms addition products with alcohols and bases, hence anhydrous $K_2CO_3$, or anhydrous $Na_2SO_4$, is employed for these classes of compounds.

Add a little of the drying agent to the ethereal soln., and allow to stand. If the drying agent absorbs sufficient water to dissolve it, run off the aq. soln., and add more of the drying agent. Before distilling, pour off the ethereal soln. from the solid drying agent. (A dry ethereal soln. should never be freely exposed to the air, as the evaporation of the ether causes a considerable deposit of moisture on the soln.)

# SCHEME I

## Compounds containing Carbon and one or more of the following elements : H, O, Metal.

Follow the appropriate procedure either under "O.S. liquid" below) or under "O.S. solid" (page 28).

***O.S. liquid.***

Carry out the instructions under (*a*) and (*b*). If O.S. is found to be viscous and miscible with water the test described under (*c*) should be applied.

(*a*) Pour 1 c.c. of O.S. into a 10-c.c. graduated cylinder (or suitably marked t.t.) and add 2 c.c. of distilled water. Close the mouth of the tube and invert two or three times. Allow to stand until the contents of the tube are clear, then note if O.S. has dissolved completely in the water or if it floats on or sinks in the water.

If O.S. has dissolved completely in twice its volume of water it will be described for the purpose of the scheme as "miscible with water" otherwise as "not miscible with water" or as a liquid which "floats on water" or "sinks in water."

(*b*) Prepare an aq. soln. of O.S. as follows :—

Make up the volume of liquid in the tube to 10 c.c. with distilled water. Close the mouth of the tube and mix the contents by inverting two or three times. If O.S. has not dissolved completely, close the mouth of the tube and shake vigorously for ½ min. ; filter if any O.S. is still undissolved. If O.S. is not miscible with water apply Class test 1 ; if O.S. is miscible with water proceed to Class test 2.

(*c*) Pour 1 c.c. of O.S. into a 10-c.c. graduated cylinder, add 1 c.c. of ether, close the mouth of the tube and invert two or three times. If O.S. is completely miscible with the ether, apply Class test 2 ; if it is not completely miscible, follow the procedure under "Polyhydric alcohols" (page 41).

### *CLASS TESTS*

(1) *Tests for phenolic compounds and for carboxylic acids not miscible with water.*

(*a*) To 2 c.c. of the *cold* prepared aq. soln. of O.S. add one drop of aq. $FeCl_3$. If a blue, violet, wine-red, red-brown, or green colour is observed, see "Phenolic compounds" (page 44); if none of these colours is obtained, then to 2 c.c. of alcohol add 3 drops of O.S. and shake round, then add 1–3 drops of aq. $FeCl_3$. If a blue, violet, wine-red, or green colour is observed, see "Phenolic compounds" (page 44); if none of these colours is obtained, apply Test (*b*).

(*b*) To 5 drops of O.S. in a t.t. add 3 c.c. of 10% aq. KOH (NaOH is not suitable as it forms a sparingly soluble sodium salt with some compounds). Close the mouth of the tube and shake vigorously for 1 min. If any O.S. has remained undissolved add 3 c.c. of water, then shake and filter the contents of the t.t. unless they consist of a gelatinous mass with a lather (suggesting that O.S. is oleic acid) in which case apply Test 3. Acidify the soln. or filtrate with conc. HCl. If a white emulsion or an oil is obtained, indicating that O.S. is either a phenol or a carboxylic acid, apply Test (*c*); if no such result is obtained, apply Test 2.

(*c*) To $\frac{1}{8}$-in. layer of solid $NaHCO_3$ in a t.t. add 5 drops of O.S. and 5 c.c. of cold water. Close the mouth of the t.t. and shake vigorously for 1 min., allowing any evolved gas to escape. Carefully acidify the soln. (previously filtered if any O.S. had remained undissolved) with conc. HCl.

If (i) a white emulsion or an oil is produced, this indicates that O.S. is a carboxylic acid or contains a carboxylic acid, probably formed by the oxidation of an aldehyde or by the hydrolysis of an ester. Apply Test 2.

(ii) no white emulsion or oil is obtained, determine the b.p. of O.S. and refer to the list of b.p.s of monohydric phenols (page 46).

(2) *Tests for aldehydes, polymers of aldehydes, acetals, and ketones.* Follow the appropriate procedure according to whether O.S. is miscible with water (below) or not miscible with water (page 27).

### *O.S. miscible with water.*

(*a*) To 2 c.c. of the *cold* prepared aq. soln. of O.S. add 2 c.c. of Schiff's reagent, shake to mix and allow to stand for *2 min.* Do not heat the mixture.

If (i) a deep violet or deep red colour is obtained, see under A (page 54).

(ii) no colour or only a faint red colour is produced, then to 2 c.c. of the prepared aq. soln. of O.S. add *one* drop of approx. 2N. HCl. Stand the t.t. in boiling water for *2 min.* (see note below), then remove it and cool the contents. Add 2 c.c. of Schiff's reagent and shake to mix. If within 2 min. a deep violet or deep red colour is obtained, see under **A** (page 54); if no colour or only a faint red colour is produced apply Test (*b*).

NOTE.

The formation of a white emulsion, changing in colour through yellow and orange to red brown, suggests that O.S. is furfuryl alcohol and Test 4 should be applied.

(*b*) Add 2 drops of O.S. to 2 c.c. of $\frac{1}{2}$% aq. soln. of sodium nitroprusside, then add approx. 2N. NaOH, drop by drop, until the soln. when tested with red litmus paper gives an alkaline reaction. (If a red colour is produced with one drop of NaOH no further addition of alkali is necessary.)

If a wine-red or orange-red colour (which soon changes to yellow) develops in a few seconds, see under **B** (page 55); if only a yellow colour develops, apply Test 3.

***O.S. not miscible with water.***

To $\frac{1}{8}$-in. layer of 2 : 4-dinitrophenylhydrazine in a dry t.t. add 2$\frac{1}{2}$ c.c. of alcohol, then add $\frac{1}{2}$ c.c. of conc. $H_2SO_4$. Warm and shake in order to dissolve all the solid. To the warm soln. add $\frac{1}{2}$ c.c. of O.S. and allow to stand for 5 min. unless a ppt. forms in a shorter period of time. (The warm $H_2SO_4$ will depolymerise a polymer of an aldehyde or hydrolyse an acetal, the liberated aldehyde will then react with the reagent.) Finally cool and shake the contents of the t.t. If a yellow, orange, or red ppt. is obtained, retain it and proceed as indicated under "O.S. not miscible with water" (page 57); if there is no ppt. apply Test 3.

(3) *Test for carboxylic acids.*

To 2 c.c. of alcohol add, using a dropping tube, one drop of O.S. and shake round, then add 1 or 2 drops of phenolphthalein soln. From a similar dropping tube add approx. $\frac{N}{10}$ NaOH, drop by drop, shaking after each addition until a red colour, which persists for 1–2 sec., is obtained, or until 10 drops of alkali have been added.

If after the addition of

(*a*) 10 drops of alkali the soln. is colourless, see "Carboxylic acids, etc." (page 67).

(*b*) 10 or fewer drops of alkali a red colour, persisting for 1–2 sec., was obtained then, if the soln. is still red, heat it to boiling and notice if the colour disappears or not. The disappearance of the red colour, either on standing or on boiling the soln., suggests that O.S. is an ester. In any case apply Test 4 as even if O.S. is an ester a hydroxyl group may also be present in the molecule.

(4) *Test for alcohols.* See caution below.

To 1 c.c. of acetyl chloride in a *dry* t.t. add about $\frac{1}{2}$ c.c. of O.S If there is no immediate reaction, watch for 2 min.

If (*a*) a vigorous reaction occurs (i.e. bubbles are freely evolved with evolution of HCl fumes, see "Alcohols" (page 33)

(*b*) there is no reaction, see "Esters, ethers, and hydrocarbons" (page 99).

CAUTION.

Alcohols, which are miscible with water, react immediately wit acetyl chloride, often with explosive violence, and the mixture ma be expelled from the tube.

NOTES.

(1) Since a reaction with acetyl chloride might be due to the presence of water in O.S. it is advisable to allow a quantity o O.S. to stand in contact with about $\frac{1}{3}$ of its volume of freshly ignited $K_2CO_3$ for $\frac{1}{2}$ hr. or more and then to repeat the test with acetyl chloride. In practice, however, it will rarely be found that members of the classes of compounds not yet detected (i.e. esters of non-hydroxy acids, ethers, and hydrocarbons) will contain sufficient water to give any appreciable reaction with acetyl chloride.

(2) With furfuryl alcohol, in addition to the vigorous reaction, the mixture becomes violet, then very dark green.

### ***O.S. solid.***

If O.S. contains a metal proceed as indicated under "Metal present" (page 31), otherwise follow the procedure below.

*No metal present.*

If O.S.

(*a*) possesses a pronounced yellow, orange, red, or green colour, see "Coloured solid compounds" (page 95).

(*b*) is an amorphous white powder, add R.G. of it to 5 c.c. of water in a t.t., heat to boiling, cool, and nearly fill the t.t. with water. Add *one* drop of iodine soln., close the mouth of the t.t. and mix the contents by inverting.

If a deep blue colour is obtained see "Starch" (page 93), or if there is no blue colour prepare an aq. soln. of O.S. in the manner described below and apply the class tests in the order given.

(*c*) does not possess the properties described under (*a*) or (*b*), prepare an aq. soln. of it in the manner described below and apply the class tests in the order given.

*Preparation of an aq. soln. of O.S.*

To a measured $\frac{1}{8}$-in layer of powdered O.S. in a dry $\frac{5}{8}$-in. t.t. add 5 c.c. of distilled water and heat to boiling. If O.S. has not dissolved completely continue boiling with shaking for ½ min. Cool the contents of the t.t. and shake vigorously.

If no solid is visible, O.S. will be described for the purpose of the scheme as "readily soluble in water"; if solid is present, O.S. will be termed "sparingly soluble in water" and the solid should be removed by filtration.

## *CLASS TESTS*

(1) *Tests for phenolic compounds and carboxylic acids.*

(*a*) To 2 c.c. of the *cold* prepared aq. soln. of O.S. add one drop of aq. $FeCl_3$.

If a blue, violet, red, or *deep* green colour is observed, see "Phenolic compounds" (page 44); if none of these colours is obtained proceed as under (i) if O.S. is readily soluble in water or as under (ii) if O.S. is sparingly soluble in water.

(i) Add R.G. of O.S. to 2 c.c. of dil. $NH_4OH$ and shake for 1 min. If an immediate yellow colour, which changes to red-brown, is observed, determine the m.p. of O.S. and see "Polyhydric phenols" (page 49); if no such colours are produced, then to a soln., obtained by boiling R.G. of O.S. with 2 c.c. of distilled water and cooling, add 5 drops of approx. $\frac{N}{10}$ NaOH, shake and then add a drop or two of phenolphthalein soln. If the soln. is colourless, proceed as indicated under "Carboxylic acids" **A** (page 70) or if a red colour is produced apply Test 2 *a*.

(ii) To ⅛-in. layer of O.S. in a t.t. add 2 c.c. of alcohol, heat just to boiling, then cool and add 1–3 drops of aq. $FeCl_3$. If a blue, violet, red, or green colour is observed, see "Phenolic compounds" (page 44); if none of these colours is obtained, apply Test (*b*).

(*b*) To ⅛-in. layer of powdered O.S. in a t.t. add 3 c.c. of approx. 2N. NaOH, close the mouth of the tube and shake vigorously for 1 min. If any O.S. has remained undissolved add 3 c.c. of water, then shake and filter the contents of the t.t. Acidify the soln. or filtrate with conc. HCl. If there is no immediate ppt., apply Test (*c*); if an immediate ppt. is obtained, indicating that O.S. is either a phenol or a carboxylic acid, then to ⅛-in. layer of powdered O.S. in a t.t. add an equal bulk of solid $NaHCO_3$ and 5 c.c. of cold water. Close the mouth of the tube and shake vigorously for 1 min., allowing any evolved gas to escape. Filter if any solid is present and carefully acidify the soln. or filtrate with conc. HCl. If a ppt. is obtained see "Carboxylic acids" under **B** (page 74); if there is no ppt. determine the m.p. of O.S and refer to the list of m.p.s of monohydric phenols (page 47)

(*c*) Add R.G. of O.S. to 2 c.c. of alcohol, heat just to boiling then cool. Add 5 drops of approx. $\frac{N}{10}$ NaOH, shake and then add 1 or 2 drops of phenolphthalein soln. If the soln is colourless, determine the m.p. of O.S. and refer to the list of m.p.s of carboxylic acids (page 76) or if a red colour is produced apply Test 2 *b*. (This test (*c*) is for the detection of higher fatty acids which would not have been indicated in the tests under (*b*).)

(2) *Tests for aldehydes, polymers of aldehydes, and ketones.*

(*a*) To 2 c.c. of the *cold* prepared aq. soln. of O.S. add 2 c.c. of Schiff's reagent, shake to mix and allow to stand for *2 min.* Do not heat the mixture. If a deep violet-red colour is produced, see under **F** (page 64); if no colour or only a faint red colour is obtained, apply Test 3.

(*b*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 5 c.c. of dil. HCl. Heat to boiling, continue boiling with shaking for 15 sec., then cool; filter if any solid is present. Add the soln. or filtrate to a soln. obtained by boiling R.G. of 2 : 4-dinitrophenylhydrazine with 2 c.c. of dil. HCl and cooling. If a ppt. is obtained, see under "Solids" (page 62) or if there is no ppt. proceed as under (*c*).

(*c*) To $\frac{1}{8}$-in. layer of O.S. in a dry t.t. add 2 c.c. of alcohol, heat just to boiling, then cool and shake. If no solid is present, use this soln. for the test given below; if solid is present, add another 3 c.c. of alcohol, heat to boiling with shaking, then cool and shake. Filter if any solid is present and use the soln. for the following test:—To $\frac{1}{8}$-in. layer of 2 : 4-dinitrophenylhydrazine in a dry t.t. add $2\frac{1}{2}$ c.c. of alcohol, then add $\frac{1}{2}$ c.c. of conc. $H_2SO_4$. Warm and shake in order to dissolve all the solid. Add the prepared alcoholic soln. of O.S. and if no ppt. is formed heat just to boiling and allow to stand for 5 min. Should no ppt. form, cool, and scrape the inside of the tube in contact with the liquid with a glass rod for a minute or so, then allow to stand for a further 5 min. If a yellow, orange, or red ppt. is obtained proceed as under "Solids" (page 62), or if there is no ppt. apply Test 4.

(3) *Tests for certain glucosides and carbohydrates*, readily soluble in water.

In a dry t.t. place R.G. of O.S. and add one drop of conc. $H_2SO_4$. If a crimson colour is produced see "Glucosides" (page 94); if no such colour is obtained apply Molisch's test for carbohydrates as follows :—Dilute the prepared aq. soln. of O.S. with an equal volume of water. To 2 c.c. of this diluted soln. add 2 drops of Molisch's reagent (a 10% soln. of α-naphthol in alcohol) and shake. Carefully pour 2 c.c. of conc. $H_2SO_4$ (contained in another t.t.) down the side of the tube and allow to stand for 2 min. If a red-violet ring is obtained where the two layers meet and on shaking the whole mixture becomes violet-red and a dull blue-violet ppt. forms, see "Carbohydrates" I (page 91); if no such result is obtained see "Solid alcohols" (pages 38, 43).

(4) *Test for certain esters, lactones, and peroxides*, sparingly soluble in water

To ⅛-in. layer of O.S. in a t.t. add 3 c.c. of 20% aq. KOH, heat to boiling and continue boiling with shaking for 1 min.

If (*a*) a deep brown or green colour is obtained, suggesting that O.S. is an ester of a polyhydric phenol, proceed as indicated under *C* (page 109).

(*b*) the liquid becomes yellow or remains colourless, cool and if any solid is present dilute with an equal volume of water and filter. Acidify the soln. or filtrate with conc. HCl; cool and shake. If there is no ppt. see "Esters, ethers, and hydrocarbons" (page 99); if a ppt. is obtained, this suggests that O.S. is a lactone, peroxide, or ester of a sparingly soluble acid, hence see "Lactones and peroxides" (page 86); or if O.S. is not one of the compounds there listed proceed as indicated under "Esters of carboxylic acids," "O.S. solid" (page 107).

*Metal present.*

*Procedure :—*

(*a*) To ⅛-in. layer of O.S. in a t.t. add 2 c.c. of dil. HCl. An effervescence of $CO_2$ indicates that O.S. is a metallic carbonate. If there is no effervescence, apply Test (*b*).

(*b*) To ⅛-in. layer of O.S. in a t.t. add 5 c.c. of distilled water and heat to boiling with shaking. Test the soln. or mixture with both blue and red litmus paper.

If an acid, neutral, or *slightly* alkaline reaction is obtained, see "Salts of carboxylic acids" (page 87). A strongly alkaline reaction will usually indicate an alkoxide (see page 43) or a phenoxide (see page 53).

# *ALCOHOLS*

These are detected by the vigorous reaction, with evolution of HCl fumes, on adding to acetyl chloride. (Test 4. Scheme I.)

*Procedure for Liquid alcohols :—*

If O.S. is

(*a*) completely miscible with twice its volume of water, pour 1 c.c. of O.S. into a dry t.t., add an equal volume of ether, close the mouth of the tube with the thumb and invert twice.

If O.S. is completely miscible with the ether, see "Monohydric Alcohols" (below) otherwise see "Polyhydric Alcohols" (page 41).

(*b*) not completely miscible with twice its volume of water, see "Monohydric Alcohols" (below).

## MONOHYDRIC ALCOHOLS

### *Liquid alcohols.*

*Procedure for the identification of O.S. :—*

Determine the b.p., then refer, in the appropriate sub-section, according to whether O.S. is completely miscible with twice its volume of water (page 33), floats on water (page 36), or sinks in water (page 37) to the list of b.p.s of alcohols. If one of these b.p.s is identical with, or near to, that of O.S., apply the tests given for that alcohol.

In many cases sufficient proof of identity will be obtained by oxidising O.S. and identifying the oxidation product; in other cases the identity of O.S. may be confirmed by the preparation (see page 267) and determination of the m.p. of a derivative.

If the properties of O.S. are not identical with those of one of the alcohols in the lists, proceed as described under "Esters of carboxylic acids" (page 100), as O.S. may be an ester of a hydroxy acid not included in the lists.

### O.S. completely miscible with twice its volume of water.

B.p.

65° Methyl alcohol. $CH_3 \cdot OH$.

(*a*) Pour 2 drops of O.S. into a dry t.t. Bend about 2 in. of stout copper wire into a compact form so

B.p. that it can be dropped into the bottom of the t.t. Heat the wire to redness and drop it into the t.t., —pungent odour of formaldehyde.

(*b*) Carry out the oxidation test (page 38).

78° Ethyl alcohol. $CH_3{\cdot}CH_2{\cdot}OH$.
82° *iso*-Propyl alcohol. $(CH_3)_2CH{\cdot}OH$.
83° *tert*-Butyl alcohol, m.p. 25°. $(CH_3)_3C{\cdot}OH$.

(*a*) To 1 c.c. of O.S. add twice the volume of 20% aq. KOH.

Complete miscibility with the aq. KOH indicates that O.S. is ethyl alcohol. Carry out the oxidation test (page 38). If O.S. floats on the aq. KOH, apply Test (*b*)

(*b*) To 2 c.c. iodine soln. add one drop of O.S., then add aq. NaOH, drop by drop, until the deep brown colour changes to pale yellow. (2–3 drops of aq. NaOH will normally be required.) The immediate formation of a pale yellow, finely divided ppt. of iodoform, with characteristic odour, indicates that O.S. is *iso*-propyl alcohol. Carry out the oxidation test (page 38).

If no ppt. is formed apply Test (*c*).

(*c*) To 1 c.c. of O.S. add 4 c.c. conc. HCl and shake.

The formation of an insoluble liquid chloride, which on standing separates as an upper layer, indicates that O.S. is *tert*-butyl alcohol.

96° Allyl alcohol. $CH_2 : CH{\cdot}CH_2{\cdot}OH$. Very pungent odour, resembling oil of mustard, irritating action on the eyes.

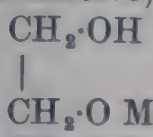
(*a*) Add 2 drops of O.S. to 5 c.c. Br water, —instant removal of brown colour, due to the presence of a double bond in the molecule of O.S.

(*b*) To 1 c.c. of O.S. add 5 c.c. dichromate mixture, —instant reduction, acrylic aldehyde (acrolein) formed with a still more irritating odour.

97° *n*-Propyl alcohol. $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH$.

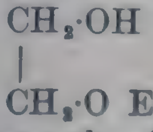
Carry out the oxidation test (page 38).

124° Ethylene glycol mono-methyl ether. (Methyl Cellosolve)



$$\begin{array}{l} CH_2{\cdot}OH \\ | \\ CH_2{\cdot}O\ Me \end{array}$$

135° Ethylene glycol mono-ethyl ether (Cellosolve)



$$\begin{array}{l} CH_2{\cdot}OH \\ | \\ CH_2{\cdot}O\ Et \end{array}$$

Carry out Tests (*a*) and (*b*) under "Ethylene glycol" (page 41), when similar results will be obtained.

B.p.

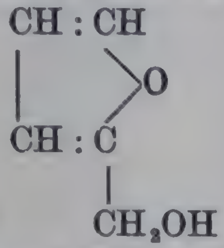
145° Methyl lactate. $CH_3·CH(OH)·COO\ Me$

154° Ethyl lactate. $CH_3·CH(OH)·COO\ Et$

(*a*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. conc. $H_2SO_4$, warm cautiously with shaking until the soln. is pale yellow, then cool. Add 2 drops of a 5% alcoholic soln. of guaiacol,
—intense red colour, indicating a lactate.

(*b*) To identify the alkyl radical proceed as described under "Esters of carboxylic acids" (page 100).

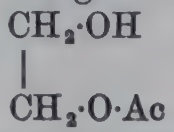
170° Furfuryl alcohol.



(*a*) Add 1 drop of O.S. to 2 c.c. dil. HCl, then gently warm and shake,
—white emulsion, changing to yellow, then orange, finally to red-brown. Dark coloured oil separates. (Due to resinification of the alcohol by the dilute acid.)

(*b*) Boil $\frac{1}{8}$-in. layer of O.S. in a t.t. and hold a wooden matchstalk, moistened with conc. HCl, in the vapour,
—matchstalk turned bluish green.

182° Ethylene glycol mono-acetate.



$$\begin{array}{l} CH_2·OH \\ | \\ CH_2·O·Ac \end{array}$$

Odourless.

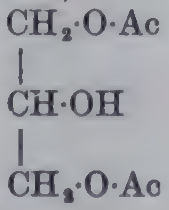
(*a*) Dissolve 1 c.c. of O.S. in 5 c.c. dil. HCl, pour the soln. into a porcelain dish, heat to boiling and continue boiling for 1 min. Add dil. $NH_4OH$ until the soln. is alkaline, boil until neutral, then cool.

To 2 c.c. of the soln. add an equal volume of aq. $FeCl_3$,
—wine-red colour (viewed through the depth of the liquid) due to the formation of $NH_4$ acetate.

(*b*) Carry out Tests (*a*) and (*b*) under "Ethylene glycol" (page 41), when similar results will be obtained.

(*c*) Percentage acetyl radical = 41·3. (For method of determination see page 43.)

260° Glyceryl diacetate (Diacetin).



$$\begin{array}{l} CH_2·O·Ac \\ | \\ CH·OH \\ | \\ CH_2·O·Ac \end{array}$$

Faint acrid odour. Somewhat viscous.

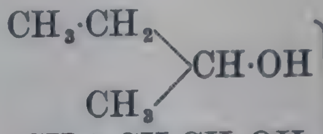
(a) Carry out Tests (a) and (b) under "Glyceryl monoacetate" (page 42), when similar results will be obtained.

(b) Percentage acetyl radical = 48·8. (For method of determination see page 43.)

**O.S. floats on water.**

B.p.

100° *sec*-Butyl alcohol.



$$\begin{matrix} CH_3{\cdot}CH_2 \\ CH_3 \end{matrix}\!\!>\!CH{\cdot}OH$$

108° *iso*-Butyl alcohol. $(CH_3)_2CH{\cdot}CH_2OH$

(a) To 2 c.c. iodine soln. add one drop of O.S., then add aq. NaOH, drop by drop, until the deep brown colour changes to pale yellow. (2–3 drops of aq. NaOH will normally be required). Allow to stand for a period of time not exceeding 2 min.

The formation (usually in about 1 min.) of a pale yellow, finely divided ppt. of iodoform, with characteristic odour, indicates that O.S. is *sec*-butyl alcohol.

(b) Carry out the oxidation test (page 38).

117° *n*-Butyl alcohol. $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH$.

Carry out the oxidation test (page 38).

131° *iso*-Amyl alcohol. $(CH_3)_2CH{\cdot}CH_2{\cdot}CH_2OH$. Disagreeable odour; provokes coughing.

Carry out the oxidation test (page 38).

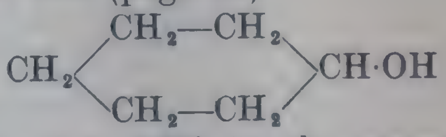
NOTE.

The amyl alcohol of commerce, obtained from fusel oil, is a mixture of *iso*-butyl carbinol, b.p. 131°, and *sec*-butyl carbinol (active amyl alcohol) b.p. 129°, both of which are primary alcohols.

138° *n*-Amyl alcohol. $CH_3{\cdot}[CH_2]_3{\cdot}CH_2OH$.

Carry out the oxidation test (page 38).

160° *cyclo*-Hexanol. (Hexalin.)



Oxidise to adipic acid, m.p. 150° in the manner described under "*cyclo*-Hexanone" (page 60).

188° *n*-Butyl lactate. $CH_3{\cdot}CH(OH){\cdot}COOC_4H_9$.

Proceed as described under "Methyl lactate" (a) and (b) (page 35).

197° Linalol. $C_{10}H_{17}{\cdot}OH$. Pleasant odour.

218° Terpineol. $C_{10}H_{17}{\cdot}OH$. Odour of lime.

222° Citronellol. $C_{10}H_{19}{\cdot}OH$. Odour of lemon rind.

230° Geraniol. $C_{10}H_{17}{\cdot}OH$. Odour of rose and geranium.

Add one drop of O.S. to $\frac{1}{8}$-in. layer in a t.t. of a soln. of Br in $CCl_4$,
—immediate decolourisation.
Pour the contents slowly out of the tube,
—no copious evolution of HBr fumes, indicating that addition, and not substitution, has occurred.

**O.S. sinks in water.**

B.p.

205° Benzyl alcohol. $C_6H_5{\cdot}CH_2OH$. Faint aromatic odour. (Unless freshly distilled possesses a slight bitter almond odour, due to the presence of benzaldehyde, formed owing to oxidation by the air).

(*a*) To 1 c.c. of O.S. in a t.t. add 1 c.c conc. HCl, shake, then immerse the end of the t.t. in boiling water,
—mixture becomes clear, and in about $\frac{1}{2}$ min. a white emulsion suddenly appears, due to the formation of benzyl chloride. On standing the benzyl chloride separates as a colourless upper layer.

(*b*) To 2 c.c. dil. $HNO_3$ (1 $HNO_3$, 4 $H_2O$) in a t.t. add one drop of O.S. and stand the t.t. in boiling water for 2 min.,
—pale yellow emulsion, and strong bitter almond odour of benzaldehyde.

(*c*) *Oxidation to benzoic acid, m.p. 121°.*

In a 100-c.c. flask place the equivalent of a $\frac{1}{4}$-in. layer in a t.t. of solid $KMnO_4$ and 30 c.c. water. Heat to boiling, allow to go just off the boil, then add 1 c.c. of O.S. Allow to stand, shaking round periodically, until the purple colour has disappeared ; cool. Filter and acidify the filtrate with conc. HCl. Filter off the solid, wash it with water, crystallise from water, dry, and determine the m.p.

220° Phenylethyl alcohol. $C_6H_5{\cdot}CH_2{\cdot}CH_2OH$. Odour of roses.

(*a*) Gives no emulsion in 1 min. when treated as described above under " Benzyl alcohol " (*a*). On removing the t.t. from the water and allowing to stand an upper layer (usually pink) is formed.

(*b*) The aromatic nature is shown by the formation of benzoic acid when oxidised in the manner described under " Cinnamyl alcohol " (*b*) (page 38).

***Solid alcohols.***

**Readily soluble in water.**

M.p.

25° *tert*-Butyl alcohol. $(CH_3)_3C{\cdot}OH$.

To 1 c.c. of molten O.S. in a t.t. add 4 c.c. conc. HCl. and shake—upper layer of *tert*-butyl chloride appears.

**Insoluble in water.**

M.p.

33° Cinnamyl alcohol. $C_6H_5{\cdot}CH : CH{\cdot}CH_2OH$, b.p. 250°. Hyacinth-like odour.

(*a*) To $\frac{1}{8}$-in. layer in a t.t. of a soln. of Br in $CCl_4$ add one drop of O.S. and shake,—deep brown colour disappears almost instantly owing to the presence of a double bond in the molecule of O.S.

(*b*) The aromatic nature is shown by the oxidation to benzoic acid, m.p. 121°, as follows :—In a 100 c.c. flask place the equivalent of a $\frac{5}{8}$-in. layer in a t.t. of solid $KMnO_4$ and 50 c.c. water. Heat to boiling, remove the flame and add gradually 1 c.c. of molten O.S., shaking round after each addition. Allow to stand, shaking round periodically, until the purple colour has practically disappeared. Cool and pass in $SO_2$ until any purple colour and the brown ppt. have disappeared. Heat to boiling, filter to remove any oil present, then cool. Filter off the solid, wash it with cold water, dry, and determine the m.p.

## OXIDATION TEST FOR ALCOHOLS

Identification of primary and secondary alcohols by recognition of the aldehyde, acid, or ketone formed by oxidation.

*Procedure* (for alcohols which are completely miscible with twice their volume of water, or which float on water) :—

Fit up an apparatus consisting of a corked 50 c.c. distilling flask connected to a water condenser.

Disconnect the flask and pour into it 1 c.c. of O.S., add two or three pieces of porous pot, then pour in 20 c.c. of dichromate mixture. Quickly cork the flask and connect it again to the condenser. Use a t.t. (marked to indicate the space occupied by 7 c.c.) as the receiver. Distil until 7 c.c. of liquid is present in the receiver, noting when 2–3 c.c. is present if there is a layer of oil on the surface of the distillate.

If O.S.

(*a*) is completely miscible with twice its volume of water, apply Schiff's test under **A**.

(*b*) floats on water, proceed as under **B** (page 40).

**A.** NOTE.

A thin layer of oil on the surface of the distillate indicates that O.S. is *n*-propyl alcohol. The distillate, however, should be shaken up and the following test applied.

*Schiff's test.*

To 1 c.c. of distillate add an equal volume of Schiff's reagent, shake to mix and allow to stand for a period of time not exceeding 2 min. (The mixture must not be heated).

If (1) a deep violet-red colour is obtained (indicating that an aldehyde has been formed and therefore O.S. is a primary alcohol) proceed with the tests under " Aldehyde present."

(2) no colour, or only a faint pink colour is obtained, apply the following *test for formic acid* :—To 1–2 c.c. of distillate add a drop of phenolphthalein soln., then add aq. NaOH, drop by drop, until a persistent red colour is obtained. Just remove the red colour by the addition of dil. HCl. Add an equal volume of aq. $HgCl_2$, heat to boiling and continue boiling for 1 min. (If a white ppt. is obtained no further boiling is necessary.)

A white ppt. of $Hg_2Cl_2$ indicates that formic acid is present in the distillate and therefore O.S. is methyl alcohol. If no ppt. is obtained proceed with the tests under " Aldehyde absent " (page 40).

*Aldehyde present.*

To 2 c.c. of distillate add an equal volume of 20% aq. KOH, shake and allow to stand for *1 min.* Note if the mixture remains clear, or if a white emulsion is formed ; in either case heat to boiling and continue boiling for ½ min.

If there is obtained

(*a*) in the cold a clear soln., and on boiling a yellow ppt., which changes to orange, with a disagreeable odour, the presence of acetaldehyde in the distillate is indicated.

Apply the following confirmatory test for acetaldehyde :—

To 2 c.c. of distillate add an equal volume of ½% aq. sodium nitroprusside, then add 1 c.c. aq. NaOH,

—wine-red colour.

The presence of acetaldehyde in the distillate indicates that O.S. is ethyl alcohol.

(*b*) in the cold a white emulsion, and on boiling a yellow colour (no orange ppt.) and a disagreeable odour, the presence of propaldehyde in the distillate is indicated. On adding to 2 c.c. of distillate an equal volume of $\frac{1}{2}$% aq. sodium nitroprusside, then 1 c.c. aq. NaOH, only an orange yellow colour will be obtained. (Difference from acetaldehyde which gives a wine-red colour.) The presence of propaldehyde in the distillate indicates that O.S. is *n*-propyl alcohol.

(*c*) a clear, colourless soln. in the cold and after boiling, apply the following test for formaldehyde :—

To 2 c.c. of distillate add R.G. of resorcinol, then pour 2 c.c. conc. $H_2SO_4$ (from another t.t.) carefully down the side of the tube,

—red ring at junction of liquids, white ppt. (which changes to violet red) forms in the aq. soln.

The presence of formaldehyde in the distillate indicates that O.S. is methyl alcohol. The test for formic acid described under 2 (page 39) should also be applied.

*Aldehyde absent.*

To 2 c.c. of distillate add an equal volume of $\frac{1}{2}$% aq. sodium nitroprusside, then add 2 drops aq. NaOH. If a wine-red colour develops, quickly acidify with acetic acid. (If the mixture is not acidified, the red colour will change to yellow.)

A wine-red colour indicates that a ketone is present in the distillate, hence O.S. is a secondary alcohol.

Wine-red colour, turned violet-red by acetic acid indicates that acetone is present in the distillate, hence O.S. is *iso*-propyl alcohol.

Wine-red colour, little affected by acetic acid, indicates that methyl ethyl ketone is present in the distillate, hence O.S. is *sec*-butyl alcohol.

For further distinction, repeat the oxidation and prepare a 2 : 4-dinitrophenylhydrazone, using the whole of the distillate. (For preparation see page 66.)

2 : 4-Dinitrophenylhydrazone of acetone m.p. 126°
,, ,, ,, ,, methyl ethyl ketone, m.p. 111°

NOTE.

*sec*-Butyl alcohol (floats on water) is included here in order to render the scheme suitable for the detection of an alcohol in aq. soln., e.g. the distillate obtained from the hydrolysis products of an ester.

**B.** A layer of oil will usually be present on the surface of the distillate.

Shake up the distillate and apply Schiff's test. (See under **A**, page 39.)

A deep violet-red colour indicates that the oil is a sparingly soluble aldehyde, hence O.S. is a primary alcohol. If no colour, or only a faint colour is obtained, proceed as indicated under "Aldehyde absent" (page 40). The presence of methyl ethyl ketone in the distillate indicates that O.S. is *sec*-butyl alcohol.

## POLYHYDRIC ALCOHOLS

***O.S. liquid.***

*Procedure for the identification of O.S.*

A determination of b.p. will not be usually worth while, owing to decomposition of O.S. at high temperature, or to the presence of water, hence apply the following test :—

To ⅛-in. layer of O.S. in a dry t.t. add $KHSO_4$ crystals to a depth of ½ in.; heat.

If there is obtained

(*a*) a pungent-smelling, highly irritating vapour (acrolein) see "Glycerol" (page 42).

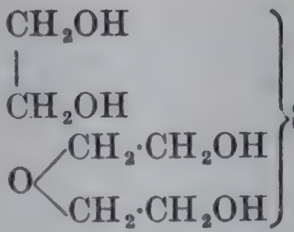
(*b*) a strong odour of acetic acid, followed on further heating by a pungent-smelling, highly irritating vapour (acrolein) see "Glyceryl mono-acetate" (page 42).

(*c*) no pungent odour, see "Ethylene glycol" and "Diethylene glycol."

B.p.

197° Ethylene glycol.

245° Diethylene glycol.



$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

$$O\begin{matrix} \diagup CH_2{\cdot}CH_2OH \\ \diagdown CH_2{\cdot}CH_2OH \end{matrix}$$

Somewhat viscous.

(*a*) Dissolve ⅛-in. layer of O.S. in a t.t. in 10 c.c. aq. $Na_2CO_3$. Pour the soln. into a boiling tube in which has been placed the equivalent of a ⅛-in. layer in a t.t. of solid $KMnO_4$. Boil for 1–2 min., then filter. (Should the filtrate be purple in colour, destroy the excess of $KMnO_4$ by the addition of $H_2O_2$.) Acidify 2 c.c. of the filtrate with glacial acetic acid; heat to boiling and add 2 or 3 drops of aq. $CaCl_2$,

—white ppt. of Ca oxalate.

(*b*) Into a dry t.t. pour 5 drops each of O.S. and conc. $H_2SO_4$ and heat until the mixture is a moderately

B.p.

deep brown colour. Cool, carefully dilute to 5 c.c. with water, then add solid NaOH with shaking until the mixture is alkaline; boil,
—characteristic, disagreeable odour of aldehyde resin.

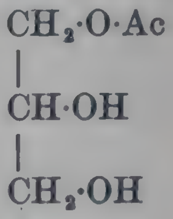
(*c*) *Preparation of a benzoyl derivative.*

Into a 100-c.c. flask pour 1 c.c. of O.S., 10 c.c. of acetone and then 5 c.c. of benzoyl chloride. Add 50 c.c. aq. NaOH (the first 10 c.c. or so gradually with cooling and shaking, then the remainder all at once); cool. Cork the flask and shake until the odour of the benzoyl chloride has practically disappeared. Filter off any solid present, wash it well with cold water, crystallise from alcohol, dry, and determine the m.p.

Ethylene glycol dibenzoate, m.p. 73°.

Diethylene glycol dibenzoate does not solidify.

decomp. Glyceryl mono-acetate (Monacetin).



$$\begin{array}{l} CH_2\cdot O\cdot Ac \\ | \\ CH\cdot OH \\ | \\ CH_2\cdot OH \end{array}$$

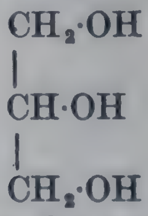
Somewhat viscous.

(*a*) See the test under "Procedure for the identification of O.S.," result (*b*), page 41.

(*b*) Dissolve 1 c.c. of O.S. in 5 c.c. dil. HCl, pour the soln. into a porcelain dish and boil for 1 min. Add dil. $NH_4OH$ until the soln. is alkaline, boil until neutral, then cool. To 2 c.c. of the soln. add an equal volume of aq. $FeCl_3$,
—wine red colour (viewed through the depth of the liquid) due to the formation of $NH_4$ acetate.

(*c*) Percentage of acetyl radical = 32·1. (For method of determination see page 43.)

290° Glycerol.



$$\begin{array}{l} CH_2\cdot OH \\ | \\ CH\cdot OH \\ | \\ CH_2\cdot OH \end{array}$$

Extremely viscous.

(*a*) See the test under "Procedure for the identification of O.S.," result (*a*), page 41.

(*b*) Dissolve ⅛-in. layer of borax in a t.t. in 20 c.c. water. To 5 c.c. of this soln. add a drop of phenolphthalein soln., then add one or two drops of O.S. and shake,

—red colour disappears; reappears on warming and disappears again on cooling.

(*c*) Prepare the benzoyl derivative in the manner described under "Ethylene glycol" (*c*), page 42.

Glyceryl tribenzoate, m.p. 76°.

***O.S. solid.***

M.p.

166° *d*-Mannitol. $CH_2OH{\cdot}[CH(OH)]_4{\cdot}CH_2OH$. Readily soluble in water; insoluble in ether.

(*a*) To 2 c.c. aq. $CuSO_4$ (Fehling's No. 1 soln. is suitable) add dil. $NH_4OH$ until a clear blue soln. is obtained, then dilute to 20 c.c. with water. To 5 c.c. of this soln. add R.G. of O.S. and shake, —ppt. forms.

(*b*) *Preparation of hexa-acetate, m.p. 119°.*

To 4 c.c. of acetic anhydride in a t.t. add 2 drops conc. $H_2SO_4$. Pour the mixture on to 1 g. of O.S. contained in a small beaker. After the violent reaction has ceased add 10 c.c. water and stir. Filter off the solid, wash it well with water, crystallise from alcohol, dry, and determine the m.p.

## DETERMINATION OF THE PERCENTAGE OF ACETYL RADICAL IN AN ALKYL ACETATE

Weigh out accurately into a 175-c.c. flask about 1 g. of the acetate.

Add 25 c.c. of approximately N. NaOH and boil gently for 15 min. Cool, add about 20 c.c. of distilled water and a few drops of phenolphthalein soln., then titrate the excess of alkali with N. HCl or $H_2SO_4$.

Also titrate similarly 25 c.c. of the NaOH soln.

If $v$ c.c. = the difference between the two titrations
and $w$ g. = the weight of acetate taken

$$\text{then percentage of acetyl radical} = \frac{43}{10} \times \frac{v \times \text{factor of acid}}{w}.$$

## ALKOXIDES (SOLIDS)

Alkoxides, i.e. Na or K derivatives of alcohols, dissolve in water, forming strongly alkaline solutions owing to hydrolysis.

Mineral acids decompose the alkoxides with liberation of the alcohol, which may be distilled over, or separated, and tested by the foregoing methods.

In any test where a mineral acid is employed, the alkoxide will give the same result as the corresponding alcohol.

# *PHENOLIC COMPOUNDS*

These are indicated by the tests given under 1 (pages 25, 29). The phenolic character should be confirmed, when possible, by the preparation of a characteristic derivative, such as an ester or an ether.

NOTE.

β-Ketonic esters and β-diketones behave like phenols.

*Procedure for the identification of O.S. :—*

Under "O.S. liquid," or "O.S. solid," in the appropriate table below, refer to the colour which has been obtained in the $FeCl_3$ test with an aqueous or alcoholic soln. and proceed as indicated.

In certain cases the odour or lack of odour, and the solubility in water of the substance, will need to be taken into account.

If directed to pages 46–51 ("Monohydric phenols" or "Polyhydric phenols"), apply any confirmatory tests, including a determination of m.p. if O.S. is a non-hygroscopic solid, given under the name of the phenol suspected. Also prepare and determine the m.p. of one of the derivatives there indicated, the first mentioned being usually the most suitable. The methods of preparation of the derivatives are given on pages 52–53.

***O.S. liquid.***

(*a*) Colour obtained by the addition of aq. $FeCl_3$ to an *aqueous* soln. of O.S.

| *Colour* | *Properties of O.S.* | |
|---|---|---|
| Blue-violet | "Carbolic" odour | See "*m*-Cresol" (page 46) |
| Blue, rapidly changing to red brown, solution becomes turbid | Tarry odour | See "Guaiacol" (page 47) |
| Red-violet | Pronounced odour | Apply "NaOH test" (page 45) |
| Wine-red<br>Red-brown | Pleasant fruity odour | Proceed as follows: |

To $\frac{1}{8}$-in. layer of neutral copper acetate in a t.t. add 5 c.c. cold water, shake well, then filter. To the filtrate add 5 drops of O.S. and shake. If a green ppt. is obtained see "β-Ketonic esters" (page 113), or if a blue ppt. is formed see "Acetylacetone" (page 60).

(*b*) Colour obtained by the addition of aq. $FeCl_3$ to an *alcoholic* soln. of O.S.

| *Colour* | *Properties of O.S.* | |
|---|---|---|
| Red-violet | Pronounced odour | Apply "NaOH test" (below) |
| Blue | Odour of cloves | See "Eugenol" (page 47) |
| Green (transient) | Odour resembling that of cloves | See "*iso*-Eugenol" (page 47) |
| " " | Odour resembling that of thyme | See "Carvacrol" (page 47) |

*NaOH test* (for liquids giving a red-violet colour with aq. FeCl$_3$).

To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. aq. NaOH and shake. If (*a*) an immediate dense white ppt. is obtained, O.S. is probably an ester of salicylic acid. See "Esters of carboxylic acid" (page 100).

(*b*) an intense yellow soln. is produced, see "Phenolic aldehydes" (page 64).

***O.S. solid.***

(*a*) Colour obtained by the addition of aq. FeCl$_3$ to an *aqueous* soln. of O.S.

| *Colour* | *Properties of O.S.* | |
|---|---|---|
| Violet blue, or blue | "Carbolic" odour | See "*o*-Cresol"<br>"*p*-Cresol"<br>"Phenol" (page 47) |
| Violet blue, or blue | Odour of vanilla<br>Sparingly soluble | Apply "Carbonyl test" (page 46) |
| Violet blue, or blue | Readily soluble in water | See "Orcinol"<br>"Resorcinol" (page 50)<br>and "Phloroglucinol" (page 51) |
| Violet | Sparingly soluble in water | Apply "Carboxyl test" (page 46) |
| Blue-black | Odourless | See "Tannic acid"<br>"Gallic acid" (page 51) |
| Blue, rapidly changing to red | Readily soluble in water | See "Pyrogallol" (page 50) |
| Blue, instantly changing to red-brown | Readily soluble in water | See "Quinol" (page 51) |
| Blue, rapidly changing to red brown. | Tarry odour | See "Guaiacol" (page 47) |
| Red-violet | | Apply "Carbonyl test" (page 46) |
| Green (changed to red with a drop of NaOH) | Readily soluble in water | See "Catechol" (page 49) |

(*b*) Colour obtained by the addition of aq. $FeCl_3$ to an *alcoholic* soln. of O.S.

| *Colour* | *Properties of O.S.* | |
|---|---|---|
| Red-violet | Sparingly soluble | Apply " Carbonyl test " (below) |
| Blue-violet | ,, ,, | See " α-Naphthol " (page 49). |
| Green | ,, ,, | See " β-Naphthol " (page 49) |
| Green (faint and transient) | Odour of thyme | See " Thymol " (page 48) |

Tests for additional groups in phenolic compounds :

*Carboxyl test.*

To $\frac{1}{8}$-in. layer of O.S. in a t.t. add an equal bulk of solid $NaHCO_3$ and 5 c.c. of cold water. Close the mouth of the t.t. and shake vigorously for 1 min., allowing any evolved gas to escape. Filter if any solid is present and carefully acidify the soln. or filtrate with conc. HCl.

If (*a*) a ppt. is obtained, this indicates the presence of a carboxyl group in the molecule of O.S. Determine the m.p. of O.S. and see Section 4 (page 79).

(*b*) there is no ppt. determine the m.p. of O.S. and refer to the list of m.p.s of monohydric phenols (page 47).

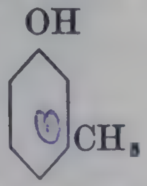
*Carbonyl test.*

To 2 c.c. of dil. HCl add R.G. of 2 : 4-dinitrophenylhydrazine, heat until the solid has dissolved, then cool. Add R.G. of O.S. and shake for a minute or so. If an orange or red ppt. is obtained see " Phenolic aldehydes " (page 64), or if there is no ppt. proceed as under " O.S. solid " (page 107)

## MONOHYDRIC PHENOLS

***Liquids.*** (See also solids of low m.p.)

B.p.
202° *m*-Cresol.



" Carbolic " odour. Sinks in water.

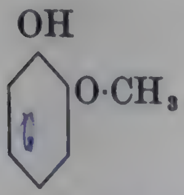
(*a*) Apply Test (*a*) under " *o*-Cresol " (page 48) when a result similar to that given by phenol and *o*-cresol will be obtained.

(*b*) Apply Test (*b*) under " *o*-Cresol " (page 48), —blue violet colour (difference from phenol and *o*-cresol which give a red colour).

Tribromo derivative, m.p. 84°.
2 : 4-Dinitrophenyl ether, m.p. 71°.
*p*-Toluenesulphonate, m.p. 50°.

B.p.

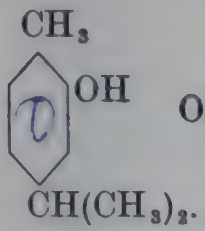
205° Guaiacol.



Tarry odour. Sinks in water.

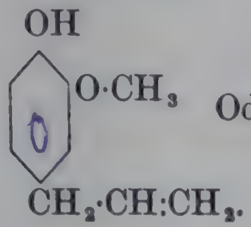
See "m.p. 28° Guaiacol" under "Solids."

237° Carvacrol.


CH₃
OH
c
CH(CH₃)₂.

Odour resembling that of thyme. Floats on water.

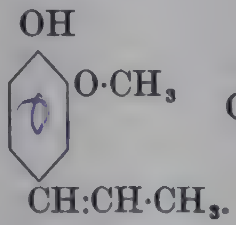
252° Eugenol.


OH
O·CH₃
o
CH₂·CH:CH₂.

Odour of cloves. Sinks in water.

Benzoate, m.p. 69°.

267° *iso*-Eugenol.


OH
O·CH₃
c
CH:CH·CH₃.

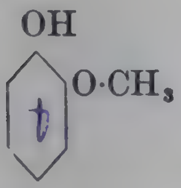
Odour resembling that of cloves. Sinks in water.

Acetate, m.p. 79°. Benzoate, m.p. 103°.

*Solids.*

M.p.

28° Guaiacol.

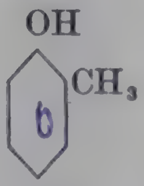


Tarry odour.

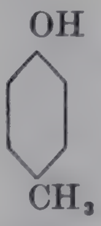
Benzoate, m.p. 57°. *p*-Toluenesulphonate, m.p. 85°

B.p.

31° *o*-Cresol. 191°



36° *p*-Cresol. 202°



42° Phenol. $C_6H_5\cdot OH$ 182°

"Carbolic" odour.

M.p.

(*a*) To R.G. of O.S. in a dry t.t. add a trace of solid sodium nitrite, then add 5 drops conc. $H_2SO_4$. Rotate the tube to mix the contents. A red colour indicates that O.S. is *p*-cresol. (Benzoate, m.p. 71°. *p*-Toluenesulphonate, m.p. 69°. 2 : 4-Dinitrophenyl ether, m.p. 93°.)

A green or blue colour indicates that O.S. is phenol or *o*-cresol. To the green or blue mixture add about 5 drops of water, then add aq. NaOH until the soln. is alkaline,—red colour on the addition of water and a blue or green colour on making alkaline (Liebermann's reaction).

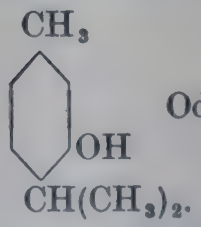
Apply Test (*b*).

(*b*) In a dry t.t. place R.G. of phthalic anhydride and twice the bulk of O.S. Add 2 drops conc. $H_2SO_4$ and gently heat until the mixture is red-brown in colour. Cool, add a few drops of water, then add aq. NaOH gradually with shaking until the mixture is alkaline. A red colour (due to the formation of phenolphthalein or its methyl derivative) indicates that O.S. is phenol or *o*-cresol. Distinguish by Test (*c*).

(*c*) To ½ c.c. of molten O.S. add 2½ c.c. conc. $NH_4OH$ and shake. Complete miscibility with the $NH_4OH$ indicates that O.S. is phenol. (Benzoate, m.p. 68°. Tribromo derivative, m.p. 93°. *p*-Toluenesulphonate, m.p. 95°. 2 : 4-Dinitrophenyl ether, m.p. 69°.)

If O.S. does not dissolve in the $NH_4OH$ this indicates that it is *o*-cresol. (2 : 4-Dinitrophenyl ether, m.p. 90°. Dibromo derivative, m.p. 56°. *p*-Toluenesulphonyl derivative, m.p. 53°. Benzoate is liquid.)

51° Thymol.



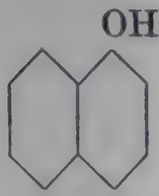
Odour of thyme

Dissolve R.G. of O.S. in 2 c.c. warm 50% acetic acid; cool. Add an equal volume of conc. $H_2SO_4$ and shake,—violet-red colour develops.

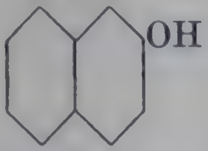
*p*-Toluenesulphonate, m.p. 71°.

M.p.

95° α-Naphthol.



122° β-Naphthol.



Faint odour

(a) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. aq. NaOH and one drop of chloroform; warm. A blue colour is obtained with both α- and β-naphthols. Distinguish by Test (b).

(b) Add R.G. of O.S. to 10 c.c. of a mixture of equal volumes of iodine soln. and aq. NaOH; shake. A *violet colour*, rapidly darkening, followed later by a ppt. indicates that O.S. is α-naphthol. (Picrate, m.p. 189°. *p*-Toluenesulphonate, m.p. 89°.)

*No change* indicates that O.S. is β-naphthol. (Acetate, m.p. 70°. Benzoate, m.p. 107°. Picrate, m.p. 156°. *p*-Toluenesulphonate, m.p. 125°.)

## POLYHYDRIC PHENOLS

*Solids.*

*General Properties.*

(1) Readily soluble in water.

(2) Easily oxidised, shown as follows :—

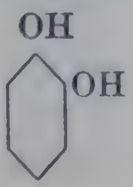
(a) Add 1 c.c. of the aq. soln. of O.S. to Tollen's reagent (1 c.c. aq. $AgNO_3$, 1 c.c. aq. NaOH; add dil. $NH_4OH$ drop by drop until a clear, colourless soln. is just obtained.)

A grey or brown ppt. is given immediately by catechol, quinol, pyrogallol, gallic acid, and tannic acid; within 30 sec. by orcinol and phloroglucinol; and within 2 min. by resorcinol.

(b) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. aq. NaOH and shake. Owing to oxidation by the air pyrogallol, tannic acid, gallic acid, and quinol yield dark red-brown solutions, other phenols yield violet, green, yellow, or brown solutions.

M.p.

104° Catechol.

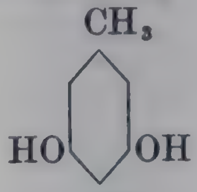


Faint odour.

M.p. To 2 c.c. of the aq. soln. of O.S. add an equal volume of lead acetate,—immediate white ppt.

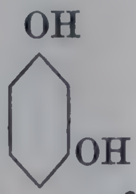
Diacetate, m.p. 63°. Dibenzoate, m.p. 84°.

107° Orcinol.



Hydrated, m.p. 58°. } Odourless.

110° Resorcinol.



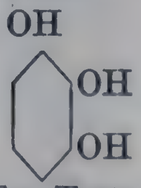
(*a*) To 1 c.c. of the aq. soln. of O.S. add 1 c.c. aq. NaOH and one drop of chloroform. Heat the mixture and when a definite red or violet-red colour is obtained fill up the t.t. with water.

A *red soln.* appearing *violet red* on shaking, yielding no fluorescence on diluting indicates that O.S. is resorcinol. Confirm the identity of O.S. by applying Test (*b*).

A *violet-red* soln. changing to deep red, yielding a green fluorescence on diluting indicates that O.S. is orcinol. (Yields no fluorescence in Test (*b*)). Dibenzoate, m.p. 88°.

(*b*) In a dry t.t. place R.G. of phthalic anhydride and twice this bulk of O.S. and then add 2 drops conc. $H_2SO_4$. Gently heat until the mixture is a red-brown colour. Cool, add a few drops of water, then add aq. NaOH gradually with shaking until the mixture is alkaline. Pour 1 c.c. of this alkaline soln. into a t.t. and fill up with water. A yellow-green fluorescence indicates that O.S. is resorcinol. Dibenzoate, m.p. 117°.

132° Pyrogallol.



Odourless.

(*a*) Apply Tests (*a*) and (*b*) under "General properties" (page 49).

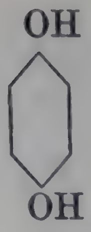
(*b*) To 2 c.c. of the aq. soln. of O.S. add 2 c.c. aq. lead acetate,—pale yellow emulsion changing to a heavy white ppt. in about 1 min.

(*c*) To 2 c.c. of the aq. soln. of O.S. add a trace of powdered $FeSO_4$ and shake,—blue-violet colour.

Triacetate, m.p. 161°.

M.p.

169° Quinol. Odourless.

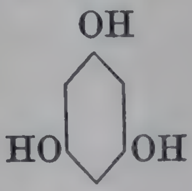


To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. dil. $H_2SO_4$, warm until the solid has dissolved, cool and add R.G. of powdered $K_2Cr_2O_7$,

—immediate ppt. of quinhydrone, consisting of green needles with a metallic lustre. Add an equal volume of dil. $H_2SO_4$ and the equivalent of $\frac{1}{8}$-in. layer in a t.t. of solid $K_2Cr_2O_7$, heat to boiling, then cool. Filter and wash the solid with a few drops of cold water,—yellow crystals of *p*-benzoquinone with peculiar pungent odour (m.p. 115°).

Diacetate, m.p. 123°. Dibenzoate, m.p. 199°.

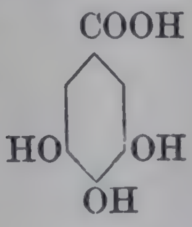
218° Phloroglucinol. Odourless.



Place $\frac{1}{2}$ in. of a wooden matchstalk in a t.t., cover it with conc. HCl and add one or two drops of the aq. soln. of O.S.,—matchstalk coloured deep red.

Triacetate, m.p. 105°. Tribenzoate, m.p. 173°.

— Gallic acid.



— Tannic acid, $C_{14}H_{10}O_9, 2H_2O$

Odourless.

(*a*) Apply Tests (*a*) and (*b*) under "General properties" (page 49).

(*b*) Add 2 c.c. of the aq. soln. of O.S. to 2 c.c. of a freshly prepared aq. soln. of gelatin.

A white ppt. indicates that O.S. is tannic acid; confirm by adding 2 c.c. of the aq. soln. of O.S. to a soln. of R.G. of quinine sulphate in 2 c.c. dil $H_2SO_4$ when a white ppt. will be obtained.

If no ppt. is produced with the gelatin soln. apply the following test for gallic acid :—To 2 c.c. of the aq. soln. of O.S. add 2 c.c. of aq. KCN,—magenta red colour.

TECHNOLOGICAL RESEA

## METHODS OF PREPARATION OF THE DERIVATIVES INDICATED UNDER THE PHENOLS IN THE FOREGOING LISTS

(See sections on "Crystallisation" and "Drying of substances," pages 16–21.)

### Acetates.

In a dry t.t. place 1 c.c. or 1 g. of O.S., add a mixture of 2½ c.c. acetic anhydride and one drop conc. $H_2SO_4$ and shake for 1 min. Pour into 10 c.c. water contained in a small beaker and stir until the oil solidifies. (If the contents of the t.t. set solid, as may occur during the acetylation of quinol or of pyrogallol, add water and stir).

Filter, wash the solid well with cold water, crystallise from a mixture of 2 pts. alcohol and 1 pt. water (use acetone for pyrogallol triacetate), dry, and determine the m.p.

### Benzoates.

In a 100-c.c. flask dissolve 1 c.c. or 1 g. of O.S. in 5 c.c. acetone (see note 2), then add 2½ c.c. benzoyl chloride. Add 50 c.c. aq. NaOH (the first 10 c.c. or so gradually with cooling and shaking, then the remainder all at once); cool. Cork the flask and shake vigorously for 10 min. (If time permits continue the shaking until the odour of the benzoyl chloride has practically disappeared.) Filter, wash the solid, first with dil. HCl, then with cold water, crystallise from alcohol (see note 1), dry, and determine the m.p.

NOTES.

(1) In the case of the benzoates of resorcinol and β-naphthol, if it is desired to crystallise the whole of the derivative, acetone will be found to be a more suitable solvent, since a large quantity of alcohol would be required.

The benzoates of quinol and phloroglucinol are only sparingly soluble in alcohol and in acetone; benzene is a suitable solvent for these derivatives.

(2) By the use of acetone a cleaner product is obtained and the phenol, especially if solid, is brought into more intimate contact with the acid chloride.

### *p*-Toluenesulphonates.

In a 100-c.c. flask place 1 c.c. or 1 g. of O.S., 2 g. of *p*-toluenesulphonyl chloride and 5 c.c. acetone. Heat on a water bath until all the solid has dissolved, then cool. Add 30 c.c. aq. NaOH, cork the flask and shake vigorously for 10 min. Filter, wash the solid with cold water and return it to the 100-c.c. flask. Add 30 c.c. aq. NaOH and some porous pot, heat to boiling and continue boiling gently for 10 min. with frequent shaking round. (By this procedure the excess of sulphonyl chloride is converted into the soluble sodium chloride and sodium *p*-toluenesulphonate, the aryl sulphonic ester being practically unaffected.) Add about an equal volume of water, cool and shake until the derivative solidifies. Filter and wash the solid well with cold water.

If, from the results of tests, O.S. is assumed to be

(*a*) phenol, guaiacol, thymol, $\alpha$-naphthol, or $\beta$-naphthol, crystallise the derivative from alcohol.

(*b*) one of the cresols, dissolve the derivative in petroleum ether, filter into a small beaker and blow air (by means of bellows) over the surface of the liquid until a sufficient quantity of the derivative crystallises out.

Dry, and determine the m.p.

**Bromo-derivatives of phenol, *o*-cresol, and *m*-cresol.**

Dissolve 1 c.c. of molten O.S. in 5 c.c. acetone, and pour the soln. into a 100-c.c. flask. Add strong Br soln. (10 c.c. Br, 15 g. KBr, 100 c.c. water) until, after shaking, the liquid is pale yellow. (About 12 c.c. will be required for *o*-cresol, and about 18 c.c. for *m*-cresol, or phenol.) Add 50 c.c. water, cool and shake vigorously. Filter, wash the solid well with cold water, crystallise from a mixture of 2 pts. alcohol and 1 pt. water, dry, and determine the m.p.

**Picrates of the naphthols.**

Dissolve $\frac{1}{8}$-in. layer of O.S. in a t.t. in 2 c.c. benzene. To the cold soln. add 2 c.c. of a saturated soln. of picric acid in benzene and shake. Filter, carefully wash the solid with a few drops of benzene, dry rapidly by placing a thin layer on filter paper and waving over a small flame, and determine the m.p.

**2 : 4-Dinitrophenyl ethers.**

In a 100-c.c. wide-mouthed flask place 1 g. of O.S., 1 g. of 2 : 4-dinitrochlorobenzene, 10 c.c. aq. $Na_2CO_3$, 20 c.c. alcohol and some porous pot. Fit the flask with a reflux condenser, heat the contents to boiling and continue boiling for 10 min. Add 30–40 c.c. water, cool and shake. Filter off the solid, wash it well with cold water, crystallise from alcohol, dry, and determine the m.p.

## PHENOXIDES

Phenoxides (phenates) dissolve in water and owing to hydrolysis yield strongly alkaline solutions. On passing $CO_2$ through the soln., or more rapidly by acidifying with dil. HCl, the phenol is liberated and may be filtered off, or extracted with ether (according to its solubility in water) and examined by the foregoing methods.

## *ALDEHYDES AND KETONES*

Included with the aldehydes are polymers and acetals which yield aldehydes on boiling with mineral acids. Samples of polymers and acetals containing a free aldehyde may be encountered.

**Liquids.**

*O.S. completely miscible with twice its volume of water.*

**A.** Aldehydes and acetals detected by Schiff's reagent (Test 2 *a*, page 26).

Procedure for the identification of acetaldehyde, methylal, and formalin.

(i) To R.G. of 2 : 4-dinitrophenylhydrazine in a t.t. add 2 c.c. of dil. HCl and heat until the solid has dissolved. Cool the soln. and add ½ c.c. of O.S. With acetaldehyde or formalin an immediate yellow ppt. of a 2 : 4-dinitrophenylhydrazone will be obtained, whereas with pure methylal a yellow ppt. (2 : 4-dinitrophenylhydrazone of formaldehyde) will be formed only after standing for a minute or two, or on warming the mixture.

The presence of a carbonyl group in the molecule of O.S. or one of its products of hydrolysis is thus indicated.

(ii) Add one drop of O.S. to Tollen's reagent (1 c.c. of aq. $AgNO_3$, 1 c.c. of aq. NaOH; add dil. $NH_4OH$ drop by drop with shaking until a clear, colourless soln. is just obtained).

An immediate grey or brown ppt. or a mirror of Ag will be obtained with acetaldehyde or formalin but not with pure methylal.

(iii) Apply Test (*a*) under "Acetaldehyde." If the soln. remains clear and colourless, apply Test (*a*) under "Formalin" and distinguish between methylal and formalin by odour and b.p.

B.p.

21° Acetaldehyde. $CH_3{\cdot}CHO$. Disagreeable, suffocating odour (in dilute aq. soln. the odour resembles that of apples).

B.p. (*a*) To 2 c.c. of the prepared aq. soln. of O.S. add 2 c.c. of 20% aq. KOH, heat to boiling and continue boiling for ½ min.—soln. becomes yellow and a yellow ppt., changing to orange, with a disagreeable odour, is obtained.

(*b*) To 2 c.c. of the prepared aq. soln. of O.S. add 2 c.c. of ½% aq. sodium nitroprusside, then add 5 drops of aq. NaOH—deep wine-red colour.

2 : 4-Dinitrophenylhydrazone, m.p. 168°. Semicarbazone, m.p. 162°.

42° Methylal. Ethereal odour.

Apply Test (*a*) under "Formalin" (below) when a similar result will be obtained as the conc. $H_2SO_4$ first hydrolyses the methylal to formaldehyde and methyl alcohol.

97°–98° Formalin (Commercial 40% aq. soln. of formaldehyde, $H{\cdot}CHO$). Pungent odour. On evaporation leaves a white residue of paraformaldehyde, $(CH_2O)n$.

(*a*) To 2 c.c. of the prepared aq. soln. of O.S. add R.G. of resorcinol, then pour 2 c.c. of conc. $H_2SO_4$ (contained in another t.t.) carefully down the side of the tube—red ring at the junction of the liquids ; white ppt., which changes to violet red, forms in the aq. layer.

(*b*) *Oxidation to formic acid, H·COOH.*

To 2 c.c. of the prepared aq. soln. of O.S. add 2 c.c. of $H_2O_2$ (20 vol.) and a drop of phenolphthalein soln., then add aq. NaOH, drop by drop with shaking, until a persistent red colour is just obtained. Stand the t.t. in boiling water for 5 min., cool, and again add aq. NaOH, drop by drop with shaking, until a persistent red colour is just obtained. Add dil. HCl until the red colour is *just* removed, then add 1 c.c. of aq. $HgCl_2$, heat to boiling and continue boiling for ½ min.

—white ppt. of $Hg_2Cl_2$ (due to the reduction of the $HgCl_2$ by the formic acid produced).

2 : 4-Dinitrophenylhydrazone, m.p. 166°.

**B.** Ketones indicated by the red colour obtained with aq. sodium nitroprusside and aq. NaOH (Test 2 *b*, page 27). All the ketones in this section give a positive result in the following test :—

*Iodoform reaction.*

To 2 c.c. of iodine soln. add one drop of O.S., then add aq.

NaOH, drop by drop with shaking, until the deep brown colour disappears,—pale yellow ppt. of iodoform, with characteristic odour.

*Procedure for the identification of O.S.*

Determine the b.p. of O.S. and refer to the following list of b.p.s of ketones. If one of these b.p.s is identical with, or near to, that of O.S., confirm the presence of a carbonyl group in the molecule and the identity of O.S. by preparing and determining the m.p. of the derivatives there indicated. For methods of preparation of derivatives, see page 66.

B.p.

56° Acetone. $\mathrm{CH_3{\cdot}CO{\cdot}CH_3}$.

2 : 4-Dinitrophenylhydrazone, m.p. 126°. Semicarbazone, m.p. 187°.

80° Methyl ethyl ketone. $\mathrm{CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_3}$.

2 : 4-Dinitrophenylhydrazone, m.p. 111°. Semicarbazone, m.p. 148°.

164° Diacetone alcohol. $\mathrm{(CH_3)_2C(OH){\cdot}CH_2{\cdot}CO{\cdot}CH_3}$. Aq. soln. neutral ; yields acetone on distillation with aq. NaOH

Into a 50 c.c. distilling flask pour 1 c.c. of O.S. and 20 c.c. of approx. 2N. NaOH and add some porous pot. Cork the flask and attach it to a water condenser. Distil, using a t.t. as the receiver, until 6–7 c.c. of distillate is obtained. From the distillate prepare acetone 2 : 4-dinitrophenylhydrazone, m.p. 126°.

165° Pyruvic acid. $\mathrm{CH_3{\cdot}CO{\cdot}COOH}$. Aq. soln. strongly acid.

In the nitroprusside + NaOH test (page 27,) a violet-red colour is obtained, changed to violet with acetic acid ; this latter colour quickly changes to yellow.

(*a*) To 2 c.c. of aq. $\mathrm{KMnO_4}$ add one drop of O.S., —purple colour changes almost immediately to brown.

(*b*) To 2 c.c. of bromine water add one drop of O.S., —immediate decolourisation.

(*c*) In a t.t. place R.G. of $\beta$-naphthol, one drop of O.S. and 2 c.c. of conc. $\mathrm{H_2SO_4}$ ; shake, —red colour becoming violet-blue on warming.

2 : 4-Dinitrophenylhydrazone, m.p. 213°.

188° Acetonyl acetone. $\mathrm{CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3}$.

2 : 4-Dinitrophenylhydrazone, m.p. 118°. Semicarbazone, m.p. 209° decomp.

*O.S. not miscible with water.*

Proceed according to whether O.S. floats on water (below) or sinks in water (page 61).

C. *O.S. floats on water.*

Add 1 or 2 drops of O.S. to 3 c.c. of Schiff's reagent and shake more or less continuously for *2 min.* Do not heat the mixture. A deep red or deep violet colour indicates that O.S. is an aldehyde, or a polymer or acetal which has yielded an aldehyde by depolymerisation or hydrolysis. Some polymers and acetals, however, will not give a positive result, while with ketones the liquid will remain colourless or only a faint red colour will be produced. If a deep red or deep violet colour is obtained, confirm the aldehydic nature of O.S. by adding one drop of it to Tollen's reagent (1 c.c. aq. $AgNO_3$, 1 c.c. aq. NaOH; add dil. $NH_4OH$, drop by drop, until a clear, colourless soln. is just obtained) and shaking for a period of time not exceeding 15 sec. A grey or brown ppt., or a mirror of Ag will be formed immediately or within 15 sec.

To identify O.S. determine its b.p. and refer to the following list of b.p.s of aldehydes, polymers of aldehydes, acetals, and ketones. If one of these b.p.s is identical with, or near to, that of O.S., confirm the identity of O.S. by filtering off, crystallising (see page 66), drying, and determining the m.p. of the 2 : 4-dinitrophenylhydrazone prepared in Test 2 (page 27).

For further confirmation of identity prepare and determine the m.p. of any other derivative indicated, or follow the given procedure. (For methods of preparation of derivatives, see page 66.)

B.p.

49° Propionaldehyde. $CH_3{\cdot}CH_2{\cdot}CHO$. Odour resembling that of acetaldehyde.

To 2 c.c. of the prepared aq. soln. of O.S. add 2 c.c. of 20% aq. KOH. Heat to boiling and continue boiling for 1 min.,—slight white ppt., dissolving to a clear pale yellow soln.; disagreeable odour. (Difference from acetaldehyde which yields an orange ppt.)

2 : 4-Dinitrophenylhydrazone, m.p. 155°.

63° *iso*-Butyraldehyde. $(CH_3)_2CH{\cdot}CHO$.

2 : 4-Dinitrophenylhydrazone, m.p. 182°.

64° Dimethylacetal. $CH_3{\cdot}CH(OCH_3)_2$

(*a*) Proceed as indicated under " Acetal " (b.p. 104°) when similar results will be obtained owing to the hydrolysis of O.S. to acetaldehyde and methyl alcohol.

(*b*) Proceed as indicated under " Acetal " but using

B.p.

20 c.c. of dichromate mixture instead of the 20 c.c. of dil. $H_2SO_4$. To 2 c.c. of the distillate add a drop of phenolphthalein soln., then add aq. NaOH drop by drop with shaking until a permanent red colour is obtained. *Just* remove the red colour by adding dil. HCl, add 1 c.c. of aq. $HgCl_2$, heat to boiling and continue boiling for 1 min.,—white ppt. of $Hg_2Cl_2$, due to the reduction of the $HgCl_2$ by the formic acid produced by the oxidation of the methyl alcohol liberated by hydrolysis of O.S.

Yields the 2 : 4-dinitrophenylhydrazone of acetaldehyde, m.p. 168°.

74° *n*-Butyraldehyde. $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$.

2 : 4-Dinitrophenylhydrazone, m.p. 122°.

80° Methyl ethyl ketone. $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_3$.

2 : 4-Dinitrophenylhydrazone, m.p. 111°. Semicarbazone, m.p. 148°.

88° Ethylal. $CH_2(OEt)_2$.

To 2 c.c. of water in a t.t. add one drop of O.S. and R.G. of resorcinol, then pour 2 c.c. of conc. $H_2SO_4$ (from another t.t.) carefully down the side of the tube,—red ring at the junction of the liquids; white ppt., which changes to violet-red, forms in the aq. soln. The conc. $H_2SO_4$ first hydrolyses O.S. to formaldehyde (detected by the above results) and ethyl alcohol.

Yields the 2 : 4-dinitrophenylhydrazone of formaldehyde, m.p. 166°.

102° Diethyl ketone. $CH_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3$.

2 : 4-Dinitrophenylhydrazone, m.p. 156°. Semicarbazone, m.p. 139°.

102° Methyl *n*-propyl ketone. $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$.

2 : 4-Dinitrophenylhydrazone, m.p. 143°. Semicarbazone, m.p. 110°.

104° Crotonaldehyde. $CH_3{\cdot}CH{:}CH{\cdot}CHO$. Pungent odour; vapour attacks the eyes.

(*a*) To 2 c.c. of the prepared aq. soln. of O.S. add 2 c.c. of 20% aq. KOH, heat to boiling and continue boiling for ½ min.,—yellow soln., followed by a yellow ppt. which changes to orange; disagreeable odour.

(*b*) To 2 c.c. of the prepared aq. soln. of O.S. add 2 c.c. of ½% aq. sodium nitroprusside, then add 5 drops of aq. NaOH,—deep wine-red colour.

B.p. 2 : 4-Dinitrophenylhydrazone, m.p. 190°. Semicarbazone, m.p. 198°.

104° Acetal. $CH_3{\cdot}CH(OEt)_2$. Odour not unpleasant; does not affect the eyes.

Into a 50-c.c. distilling flask pour 1 c.c. of O.S. and 20 c.c. of dil. $H_2SO_4$ and add some porous pot. Cork the flask and attach it to a water condenser. Distil, using a t.t. as the receiver, until 6–7 c.c. of distillate is obtained. Test the distillate for acetaldehyde (produced together with ethyl alcohol by hydrolysis) as follows :—

(*a*) To 2 c.c. add 2 c.c. of 20% aq. KOH, heat to boiling and continue boiling for ½ min.,—yellow soln., followed by a yellow ppt., changing to orange; disagreeable odour.

(*b*) To 2 c.c. add 2 c.c. of ½% aq. sodium nitroprusside, then add 5 drops of aq. NaOH,—wine-red colour.

Yields the 2 : 4-dinitrophenylhydrazone of acetaldehyde, m.p. 168°.

124° Paraldehyde. $(C_2H_4O)_3$.

Proceed as described above under "Acetal" when similar results will be obtained as the distillation with dil. $H_2SO_4$ converts paraldehyde into acetaldehyde.

Yields the 2 : 4-dinitrophenylhydrazone of acetaldehyde, m.p. 168°.

124° Di-*iso*propyl ketone. $(CH_3)_2CH{\cdot}CO{\cdot}CH(CH_3)_2$.

2 : 4-Dinitrophenylhydrazone, m.p. 93°. Semicarbazone, m.p. 157°.

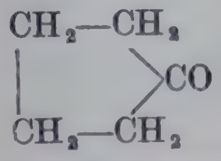
130° Mesityl oxide. $CH_3{\cdot}CO{\cdot}CH{=}C(CH_3)_2$.

(*a*) Apply the iodoform reaction (page 55) when a positive result will be obtained.

(*b*) To ⅛-in. layer in a t.t. of a soln. of Br in $CCl_4$ add 2 drops of O.S.,—immediate decolourisation, due to the presence of a double bond in the molecule of O.S.

2 : 4-Dinitrophenylhydrazone (red: crystallise from glacial acetic), m.p. 200°. Semicarbazone, m.p. 164°.

130° *cyclo*-Pentanone.



2 : 4-Dinitrophenylhydrazone (yellow), m.p. 146°. Semicarbazone, m.p. 203° decomp.

B.p.

139° Acetylacetone. $CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_3$.

Aq. soln. gives a red-brown colour with aq. $FeCl_3$. Gives a blue ppt. with neutral copper acetate soln.

(*a*) Apply Test 2 *b* (page 27) when a wine-red colour will be obtained.

(*b*) Distil 1 c.c. of O.S. with 20 c.c. of approx. 2N. NaOH and collect 6–7 c.c. of distillate. From the distillate (consisting of aqueous acetone) prepare acetone 2 : 4-dinitrophenylhydrazone, m.p. 126°, by Method 1 (page 66).

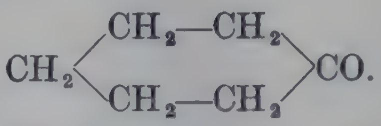
151° Methyl *n*-amyl ketone. $CH_3\cdot CO\cdot[CH_2]_4\cdot CH_3$.

2 : 4-Dinitrophenylhydrazone, m.p. 70°. Semicarbazone, m.p. 124°.

154° *n*-Heptaldehyde (Oenanthol). $CH_3[CH_2]_5\cdot CHO$. Unpleasant odour.

2 : 4-Dinitrophenylhydrazone, m.p. 106°. Semicarbazone, m.p. 109°.

155° *cyclo*-Hexanone.



2 : 4-Dinitrophenylhydrazone, m.p. 160°. Semicarbazone, m.p. 166°.

*Oxidation to adipic acid, m.p. 150°.*

Into a 100 c.c. flask pour 1 c.c. of O.S. and 30 c.c. of dichromate mixture, heat to boiling and continue boiling gently for 5 min. Cool, filter and carefully wash the solid free from green chromium salt with cold water (adipic acid is moderately soluble in cold water). Crystallise the solid from water, dry, and determine the m.p.

172° Methyl *n*-hexyl ketone. $CH_3\cdot CO\cdot[CH_2]_5\cdot CH_3$.

2 : 4-Dinitrophenylhydrazone, m.p. 67°. Semicarbazone, m.p. 123°

204° *d*-Citronellal. $C_9H_{17}\cdot CHO$. Odour of lemon rind.

Semicarbazone, m.p. 84°.

207° *l*-Menthone. $C_{10}H_{18}O$. Odour of peppermint.

2 : 4-Dinitrophenylhydrazone, m.p. 146°.

228° Citral, $C_9H_{15}\cdot CHO$. Odour of lemon.

The natural aldehyde is a mixture of two geometrical isomers.

230° *d*-Carvone, $C_{10}H_{14}O$. Odour of carraway.

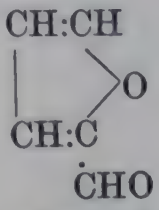
2 : 4-Dinitrophenylhydrazone, m.p. 189.

). ***O.S. sinks in water.***

Determine the b.p. of O.S. and refer to the following list of b.p.s f aldehydes and ketones. If one of these b.p.s is identical with, r near to, that of O.S. confirm the identity of O.S. by preparing nd determining the m.p. of one or more of the derivatives there ndicated. (For preparation of derivatives, see page 66.)

B.p.

161° Furfural.



Odour somewhat resembling bitter almonds. Colourless when pure; becomes brown with age.

(*a*) Dip the end of a roll of filter paper into a mixture of equal volumes of glacial acetic acid and aniline and remove any excess of the mixture by pressing the end of the roll between filter paper. Boil a mixture of one drop of O.S. and 2 c.c. of water in a t.t. and hold the end of the roll in the vapours, —paper turned deep red.

(*b*) Add 2 drops of O.S. to 1 c.c. of Fehling's soln. (equal volumes of No. 1 and No. 2) and boil for ½ min.,
— red ppt. of $Cu_2O$.

Phenylhydrazone, m.p. 97°. Semicarbazone, m.p. 202°.

179° Benzaldehyde. $C_6H_5{\cdot}CHO$. Odour of bitter almonds.

(*a*) *Preparation of benzoin*, $C_6H_5{\cdot}CH(OH){\cdot}CO{\cdot}C_6H_5$, m.p. 134°.

Dissolve a piece of KCN, about the size of a pea, in 1 c.c. of water in a t.t. Add 3 c.c. of alcohol and 10 drops of O.S. Stand the t.t. for 5 min. in about 200 c.c. of water, which has been heated to boiling and from which the flame has been removed. Cool, add 5 c.c. of water, shake and filter. Wash the solid with water, crystallise it twice from alcohol, dry, and determine the m.p.

(*b*) *Preparation of dibenzalacetone*, $(C_6H_5{\cdot}CH{:}CH)_2CO$, m.p. 112°. (Pale yellow lustrous plates).

Into a boiling-tube pour 1 c.c. of O.S., 5 drops of acetone, 5 c.c. of alcohol, and 2 c.c. of aq. NaOH. Heat the mixture to boiling, continue boiling for 1 min., then cool and shake vigorously. Add 20 c.c. of water; shake and filter. Wash the yellow solid with cold water, crystallise it twice from alcohol, dry, and determine the m.p.

B.p.

Phenylhydrazone, m.p. 156°. Semicarbazone, m.p. 214°.

193° Phenylacetaldehyde. $C_6H_5{\cdot}CH_2{\cdot}CHO$.

2 : 4-Dinitrophenylhydrazone, m.p. 121°. Semicarbazone, m.p. 153°.

202° Acetophenone. $C_6H_5{\cdot}CO{\cdot}CH_3$.

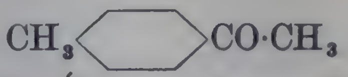
Add a drop of O.S. to 2 c.c. of ½% aq. soln. of sodium nitroprusside, then add 2 drops of aq. NaOH, —wine-red colour, turned blue on acidifying with acetic acid.

Semicarbazone, m.p. 198°. Phenylhydrazone, m.p. 103° (turns brown and shrinks at 100°).

210° Propiophenone. $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_3$.

Semicarbazone, m.p. 174°. 2 : 4-Dinitrophenylhydrazone, m.p. 191°.

225° *p*-Methylacetophenone.

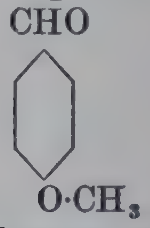


Apply the test under "Acetophenone" (page 62) when a similar result will be obtained. Semicarbazone, m.p. 205°.

247° Cinnamaldehyde. $C_6H_5{\cdot}CH{:}CH{\cdot}CHO$. Odour of cinnamon.

Phenylhydrazone (yellow), m.p. 168°. Semicarbazone, m.p. 215°.

248° Anisaldehyde



Phenylhydrazone (white), m.p. 120°. Semicarbazone, m.p. 203°.

*Oxidation to anisic acid, m.p. 184°.*

In a 250-c.c. flask place the equivalent of ¼-in. layer in a t.t. of solid $KMnO_4$ and 50 c.c. of water. Heat to boiling, allow to go just off the boil and add 1 c.c. of O.S. Gently shake round (it is not necessary to heat further) until the colour of the $KMnO_4$ has disappeared; cool. Filter, and acidify the filtrate with conc. HCl. Filter off the solid, wash it with water, crystallise from alcohol, dry, and determine the m.p.

***Solids.***

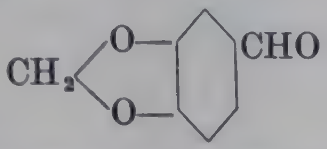
Proceed as indicated below under **E** unless a yellow ppt. was obtained in Test 2 *b* (page 30), in which case ascertain first if O.S. is one of the compounds described under **F** (page 64).

E.

Determine the m.p. of O.S. and refer to the following list of m.p.s of aldehydes and ketones. If one of these m.p.s is identical with, or near to, that of O.S. confirm the identity of O.S. by preparing and determining the m.p. of one or more of the derivatives there indicated. (The methods of preparation of the derivatives, if not given under the name of the aldehyde or ketone, will be found on pages 65–66.)

M.p.

37° Piperonal.



(*a*) *Preparation of oxime, m.p. 110°.*

Dissolve ½ g. of O.S. in 2 c.c. of alcohol in a t.t. and add a soln. of ½ g. of hydroxylamine hydrochloride and 1 g. of crystallised sodium acetate in 2 c.c. of water. Stand the t.t. for 10 min. in about 200 c.c. of water which has been heated to boiling and from which the flame has been removed. Cool, filter off the solid, wash it with cold water, crystallise from dilute alcohol, dry, and determine the m.p.

(*b*) *Oxidation to piperonylic acid*, m.p. 228°.

Oxidise the equivalent of ¼-in. layer of O.S. in a t.t. in the manner described for "Anisaldehyde" (page 62). Crystallise the acid obtained from dilute alcohol, dry, and determine the m.p.

Phenylhydrazone, m.p. 100°. Semicarbazone, m.p. 230°.

48° Benzophenone (Diphenyl ketone). $C_6H_5{\cdot}CO{\cdot}C_6H_5$.

*Preparation of oxime*, m.p. 141°.

In a 100-c.c. wide-mouthed flask place ½ g. of hydroxylamine hydrochloride, 1 g. of solid KOH, and 5 c.c. of water. Add a soln. of ½ g. of O.S. in 5 c.c. of alcohol and some porous pot. Fit the flask with a reflux water condenser, heat the contents to boiling and continue boiling gently for ½ hr. (a better yield of oxime will be obtained if the boiling is continued for 1 hr.). Cool, add 20 c.c. of water and shake. Filter from unchanged ketone and add to the filtrate dil. HCl until the mixture is just acid. Filter off the pptd. oxime, wash it with water, crystallise from dilute alcohol, dry, and determine the m.p.

Phenylhydrazone, m.p. 137°.

M.p.

55° Deoxybenzoin. $C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}C_6H_5$.

2 : 4-Dinitrophenylhydrazone, m.p. 195°.

59° Phenyl-*p*-tolyl ketone. $C_6H_5{\cdot}CO{\cdot}C_6H_4{\cdot}CH_3$.

2 : 4-Dinitrophenylhydrazone, m.p. 199°.

134° Benzoin. $C_6H_5{\cdot}CH(OH){\cdot}CO{\cdot}C_6H_5$.

(*a*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 1 c.c. of Fehling's soln. (equal volumes of No. 1 and No. 2) and 1 c.c. of water. Heat to boiling and continue boiling for $\frac{1}{2}$ min.,

—red ppt. of $Cu_2O$.

(*b*) *Oxidation to benzil,* $C_6H_5{\cdot}CO{\cdot}CO{\cdot}C_6H_5$, *m.p. 95°.*

To $\frac{1}{2}$ g. of O.S. in a dry t.t. add 1·25 c.c. of conc. $HNO_3$ (a larger volume of $HNO_3$ may cause nitration) and stand the t.t. in gently boiling water for 10 min. Cool, add 10 c.c. of water and shake until the red oil solidifies. Filter off the solid, wash it with cold water, crystallise twice from alcohol, dry, and determine the m.p.

Acetate, m.p. 83°, see "Vanillin triacetate," page 65).

179° *d*-Camphor. $C_{10}H_{16}O$.

2 : 4-Dinitrophenylhydrazone, m.p. 177°.

**F.** Solid polymers of aliphatic aldehydes.

Paraformaldehyde. $(CH_2O)n$. Pungent, fishy odour.

Apply the tests under "Formalin" (page 55) when similar results will be obtained.

Metaldehyde. $(C_2H_4O)n$.

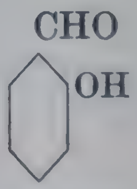
Proceed as under "Acetal" (page 59) using the equivalent of $\frac{1}{4}$-in. layer of O.S. in a t.t., when similar results will be obtained.

**G.** Phenolic aldehydes.

***Liquids.***

B.p.

196° Salicylaldehyde.



To a solution of R.G. of 2 : 4-dinitrophenylhydrazine in 1 c.c. of alcohol add 2 drops of conc. $H_2SO_4$ and one drop of O.S.,

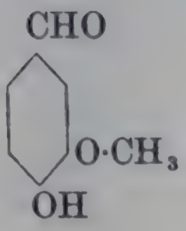
—orange ppt. indicating the presence of a carbonyl group in the molecule of O.S.

Phenylhydrazone (greenish-yellow), m.p. 142° ; semicarbazone, m.p. 229° (see page 66).

### *Solids.*

M.p.

80° Vanillin.



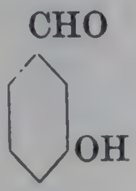
Odour of vanilla.

*Preparation of triacetate, m.p. 88°.*

To ¼-in. layer of O.S. in a dry t.t. add a mixture of 4 c.c. of acetic anhydride and 2 drops of conc. $H_2SO_4$. Shake until all the solid has dissolved, then add 10 c.c. of water and cool. Allow to stand, shaking periodically, until the oil solidifies. Filter off the solid, wash it with cold water, crystallise from alcohol, dry, and determine the m.p.

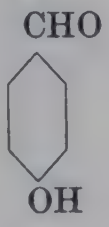
Semicarbazone, m.p. 229° (see page 66).

104° *m*-Hydroxybenzaldehyde.



Triacetate. m.p. 76°

115° *p*-Hydroxybenzaldehyde.



Triacetate, m.p. 93°

See " Vanillin triacetate " (page 65).

### *Preparation of derivatives.* (See also pages 16–21.)

### **Phenylhydrazones.**

*O.S. liquid.*

To 2 c.c. of 50% acetic acid add 5 drops of phenylhydrazine, heat just to boiling, add 5 drops of O.S. and shake. Add 5 c.c. of water, shake vigorously and cool. Filter, etc., as under " O.S. solid."

***O.S. solid.***

To $\frac{1}{4}$-in. layer of O.S. in a dry t.t. add 1 c.c. of glacial acetic acid and heat until solution is complete. Add 5 drops of phenylhydrazine and heat just to boiling, then cool.

If no solid separates, scrape the glass in contact with the liquid with a glass rod in order to assist precipitation. When solid has separated add 5 c.c. of water and stir. Filter off the solid phenylhydrazone, wash it with cold water and crystallise twice from alcohol (or aqueous alcohol). Dry a thin layer on filter paper over a small flame and determine the m.p. (Many phenylhydrazones decompose on prolonged heating in a steam oven, or on keeping.)

### 2 : 4-Dinitrophenylhydrazones.

METHOD 1. For aldehydes and ketones miscible with water.

To $\frac{1}{8}$-in. layer of 2 : 4-dinitrophenylhydrazine in a dry t.t. add 10 c.c. of dil. HCl and heat until all the solid has dissolved. Cool the soln., add $\frac{1}{2}$ c.c. of O.S. and shake. Filter off the solid, wash it with cold water, crystallise from alcohol, dry, and determine the m.p.

METHOD 2. For aldehydes and ketones not miscible with water.

Follow the procedure under "O.S. not miscible with water" (page 27) if O.S. is a liquid or if O.S. is a solid proceed as indicated in Test 2 *c* (page 30). Filter off the ppt., wash it with cold alcohol, crystallise from alcohol (or glacial acetic acid if sparingly soluble in alcohol), dry, and determine the m.p.

### Semicarbazones.

In a dry t.t. place $\frac{1}{4}$-in. layer each of semicarbazide hydrochloride and powdered crystallised sodium acetate. Add 1 c.c. of water and heat until the solid has dissolved, then add $\frac{1}{2}$ c.c. of O.S. and shake.

If O.S. has

(*a*) mixed with the reagent, cool, filter off the solid, very carefully wash it with cold water, crystallise from methyl alcohol, dry, and determine the m.p.

(*b*) not mixed with the reagent, add 1 c.c. of alcohol.

If the contents of the t.t.

  (i) have set to a solid mass, add 5 c.c. of water and stir. Filter off the solid, wash it with water, crystallise from alcohol (or glacial acetic acid if sparingly soluble in alcohol), dry, and determine the m.p.

  (ii) have not set to a solid mass, warm until a clear soln. is obtained, adding if necessary more alcohol. Cool, add 5 c.c. of water and stir. Filter off the solid, wash it with cold water, crystallise from alcohol (or dilute alcohol), dry, and determine the m.p.

# *CARBOXYLIC ACIDS, ETC.*

IMPORTANT GENERAL NOTES.

(1) Acid anhydrides and certain esters (acid esters, also methyl and ethyl formates, methyl lactate, methyl and ethyl oxalates) in addition to carboxylic acids, yield strongly acid aqueous solutions.

(2) For certain tests an aqueous soln. of a neutral salt of an acid is required. Prepare as follows :—

To $\frac{1}{8}$-in. layer of the acid in a t.t. add just sufficient dil. $NH_4OH$ to yield an alkaline soln. and dilute to 10 c.c. with distilled water. Pour the soln. into a dish and boil until a piece of red litmus paper momentarily immersed in the soln. is just no longer turned blue, keeping the volume between 5 c.c. and 10 c.c. by the addition, when necessary, of distilled water. Finally cool and make up the volume to 10 c.c. with distilled water.

(3) The determination of the equivalent weight of an acid or anhydride is a valuable aid to identification. (For methods of determination see page 81.)

*Procedure for the identification of O.S. :—*

If O.S. is a liquid follow the procedure given below ; if a solid follow the procedure under "O.S. solid" (page 69).

***O.S. liquid.***

If O.S.

(i) is miscible with water, then to a soln. of one drop of O.S. in 2 c.c. of water add 3 drops of aq. $FeCl_3$. If a strong yellow colour is produced, see "Lactic acid" (page 73) ; if no such colour is obtained, apply the tests under "Formic acid, etc." (page 68) unless the odour of O.S. is like that of rancid butter in which case see "*n*-Butyric acid" (page 68).

(ii) floats on water, or sinks in water, determine the b.p. and refer to the appropriate list of b.p.s of compounds (page 69).

(iii) is not identifiable as one of the compounds in the following lists proceed as indicated under "Esters of carboxylic acids" (page 100).

**O.S. completely miscible with twice its volume of water.**

| B.p. | | | | *Equiv. wt.* |
|---|---|---|---|---|
| 100° | Formic acid. | $H{\cdot}COOH$ | Pungent odour. Miscible with water. | 46·02. |
| 118° | Acetic acid. | $CH_3{\cdot}COOH$ | | 60·03. |
| 140° | Propionic acid. | $CH_3{\cdot}CH_2{\cdot}COOH$ | | 74·05. |

(*a*) To 2 c.c. of the neutral aq. soln. add an equal volume of aq. $FeCl_3$. A wine-red colour (viewed through the depth of the liquid), yielding a reddish brown ppt. on boiling, is given by all three acids. Apply Test (*b*).

(*b*) To 2 c.c. of the neutral aq. soln. add 1 c.c. aq. $HgCl_2$, heat to boiling and continue boiling for $\frac{1}{2}$ min. If no ppt. is obtained apply Test (*c*). A white ppt. ($Hg_2Cl_2$) indicates that O.S. is formic acid (or a formate). Apply the following confirmatory tests :—

(i) To $\frac{1}{8}$-in. layer of O.S. in a dry t.t. add 5 drops conc. $H_2SO_4$. Gently warm the mixture by rotating the end of the tube over a small flame and turn the mouth of the tube periodically to the flame. CO is evolved and burns with a characteristic blue flame.

(ii) To 2 c.c. of the neutral aq. soln. add an equal volume of aq. $AgNO_3$ and boil,
—liquid becomes brown, then a grey ppt. of silver appears.

(*c*) To 2 c.c. of the neutral aq. soln. add 2 drops aq. $FeCl_3$ and then add 1 c.c. of amyl alcohol. Shake vigorously and allow to stand until the mixture separates into two layers. The transference of the red-brown colour from the aqueous to the alcohol layer indicates that O.S. is propionic acid (or a propionate). No coloration of the amyl alcohol indicates that O.S. is acetic acid (or an acetate). Apply the following test for acetic acid (or an acetate) :—To $\frac{1}{8}$-in. layer of O.S. in a dry t.t. add 10 drops absolute alcohol and 10 drops conc. $H_2SO_4$. Heat gently, cool and pour into 5 c.c. water contained in a dish—pleasant fruity odour of ethyl acetate.

162° *n*-Butyric acid. $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$. Equiv. wt. 88·06. Odour of rancid butter.

**O.S. floats on water.**

B.p.

155° *iso*-Butyric acid. $(CH_3)_2CH{\cdot}COOH$. Equiv. wt. 88·06.

176° *iso*-Valeric acid. $(CH_3)_2CH{\cdot}CH_2{\cdot}COOH$. Equiv. wt. 102·1.

186° *n*-Valeric acid. $CH_3{\cdot}[CH_2]_3{\cdot}COOH$. Equiv. wt. 102·1.

205° *n*-Caproic acid. $CH_3{\cdot}[CH_2]_4{\cdot}COOH$. Equiv. wt. 116·1.

223° *n*-Heptoic acid. $CH_3{\cdot}[CH_2]_5{\cdot}COOH$. Equiv. wt. 130·1.

237° *n*-Caprylic acid. $CH_3{\cdot}[CH_2]_6{\cdot}COOH$. Equiv. wt. 144·1.

253° Pelargonic acid. $CH_3{\cdot}[CH_2]_7{\cdot}COOH$. Equiv. wt. 158·1.

269° Capric acid. $CH_3{\cdot}[CH_2]_8{\cdot}COOH$. Equiv. wt. 172·1.

— Oleic acid. $CH_3{\cdot}[CH_2]_7{\cdot}CH : CH{\cdot}[CH_2]_7{\cdot}COOH$. Usually possesses a tallow-like odour. Equiv. wt. 282·3.

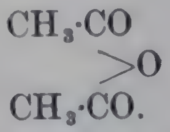
To $\frac{1}{8}$-in. layer in a t.t. of a soln. of Br in $CCl_4$ add one drop of O.S.,

—deep brown colour immediately removed, owing to the presence of a double bond in the molecule of the acid.

**O.S. sinks in water.**

B.p.

138° Acetic anhydride.



$$\begin{matrix} CH_3{\cdot}CO \\ & >O \\ CH_3{\cdot}CO. \end{matrix}$$

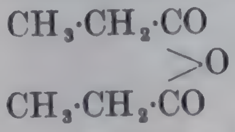
Pungent, irritating odour.

Equiv. wt. 51·02. Converted into acetic acid by boiling with water.

*Preparation of anilide, m.p.* 114°, and p-*toluidide, m.p.* 148° :—

In a dry boiling-tube place $\frac{1}{2}$ c.c. of freshly distilled aniline (or $\frac{1}{2}$ g. *p*-toluidine) and add 1 c.c. of O.S. When the reaction has ceased add 20 c.c. boiling water and boil until the lower layer has completely dissolved. (In the case of the *p*-toluidide it will be necessary to add a little glacial acetic acid in order to effect complete solution). Cool, filter, wash the solid with cold water, dry, and determine the m.p.

168° Propionic anhydride.



$$\begin{matrix} CH_3{\cdot}CH_2{\cdot}CO \\ & >O \\ CH_3{\cdot}CH_2{\cdot}CO \end{matrix}$$

Pungent odour.

Equiv. wt. 65·04. Converted into propionic acid by boiling with water.

Anilide, m.p. 105°. *p*-Toluidide, m.p. 124°. (For preparation, see under " Acetic anhydride.")

186° Diethyl oxalate. See " Esters " (page 100).

***O.S. solid.***

If O.S. is readily soluble in water, proceed as indicated under **A** : if sparingly soluble as under **B** (page 74).

A.

(*a*) To 2 c.c. of the prepared aq. soln. of O.S. add a drop of phenolphthalein soln., then add $\frac{N}{1}$ NaOH until after shaking a red colour is just obtained. Heat just to boiling. (If the red colour disappears this indicates that O.S. is an ester.) Add half the volume of glacial acetic acid, heat to boiling, then add 2–3 drops of aq. $CaCl_2$.

If (i) no ppt. is obtained apply Test (*b*).

(ii) an immediate white ppt. is obtained this indicates that O.S. is oxalic acid, or, if the red colour disappeared on boiling, dimethyl oxalate (see below). Both substances give a positive result in the following test :—

To $\frac{1}{8}$-in. layer of O.S. in a dry t.t. add 5 drops conc. $H_2SO_4$. Gently warm the mixture by rotating the end of the tube over a small flame, and turn the mouth of the tube periodically to the flame. CO is evolved and burns with a characteristic blue flame.

Oxalic acid. $\begin{array}{l}COOH\\ COOH\end{array}$

Equiv. wt. 45·01 (anhydrous); 63·02 (+ $2H_2O$).

Dimethyl oxalate, $\begin{array}{l}COO\cdot CH_3\\ \dot{C}OO\cdot CH_3\end{array}$, m.p. 54°.

The methyl radical may be detected by proceeding as indicated under "Details of method of hydrolysis" (page 100). Use 2 g. of O.S. and 10 c.c. of 20% aq. KOH. Hydrolysis will be complete in 5 min.

(*b*) To 2 c.c. of the prepared aq. soln. of O.S. (and also to an equal volume of an aq. soln. of tartaric acid of similar strength) add 3 drops aq. $FeCl_3$.

If with the aq. soln. of O.S. there is obtained

(i) a strong yellow colour (like that obtained with the tartaric acid) with no ppt. proceed as indicated under Section 2 (page 72).

(ii) a yellow ppt., a practically colourless soln., or a reddish brown soln. proceed as indicated under Section 1.

Section 1.

*Preliminary Test.*

To 2 c.c. of the aq. soln. of O.S. add an equal volume of aq. $KMnO_4$ and shake for $\frac{1}{2}$ min.

If the purple colour

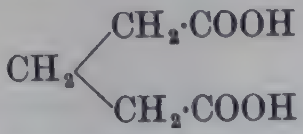
(i) is unaltered see "Saturated acids and anhydrides" (page 71).

(ii) is changed to brown see "Unsaturated acids and anhydrides" (page 72).

In either case determine the m.p. of O.S. and refer to the list of m.p.s of acids and anhydrides. If one of these m.p.s is identical with, or near to, that of O.S. confirm the identity of O.S. by applying any tests given.

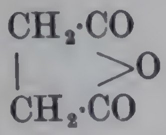
**Saturated acids and anhydrides.**

M.p.



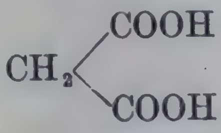
97° Glutaric acid. $CH_2<\begin{matrix}CH_2\cdot COOH\\ CH_2\cdot COOH\end{matrix}$ Equiv. wt. 66·03.

Apply the test under "Succinic acid" when a similar result will be obtained. *p*-Nitrobenzyl ester, m.p. 69°.



119° Succinic anhydride. $\begin{matrix}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{matrix}>O$ Equiv. wt. 50·02.

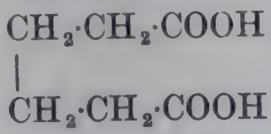
Apply the test under "Succinic acid" when a similar result will be obtained.



133° Malonic acid. $CH_2<\begin{matrix}COOH\\ COOH\end{matrix}$ Equiv. wt. 52·02.

(*a*) Heat $\frac{1}{8}$-in. layer of O.S. in a dry t.t. until the solid has melted and effervescence occurs (due to the evolution of $CO_2$)—sharp odour of acetic acid.

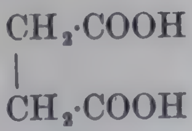
(*b*) To $\frac{1}{8}$-in. layer of O.S. in a dry t.t. add 2 c.c. acetic anhydride and boil,—reddish yellow liquid with yellowish green fluorescence. *p*-Nitrobenzyl ester, m.p. 85°.



150° Adipic acid. $\begin{matrix}CH_2\cdot CH_2\cdot COOH\\ |\\ CH_2\cdot CH_2\cdot COOH\end{matrix}$ Equiv. wt. 73·04.

Apply the test under "Succinic acid",—violet-red colour after rendering the mixture alkaline with NaOH.

Amide, m.p. 220° (see page 80). *p*-Nitrobenzyl ester, m.p. 106°.



185° Succinic acid. $\begin{matrix}CH_2\cdot COOH\\ |\\ CH_2\cdot COOH\end{matrix}$ Equiv. wt. 59·02.

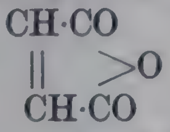
Place R.G. of O.S. in a dry t.t. and add twice the bulk of resorcinol and 2 drops conc. $H_2SO_4$. Gently heat until the mixture is a red-brown colour. Cool, add a few drops of water, then add aq. NaOH until the mixture is alkaline. Pour

1 c.c. of the alkaline soln. into a t.t. and fill up with water,—yellow-green fluorescence.

*p*-Nitrobenzyl ester, m.p. 88° (see page 232). Anilide, m.p. 226° (see page 80).

**Unsaturated acids and anhydrides.**

M.p.

56° Maleic anhydride. 

$$\begin{array}{l}\mathrm{CH{\cdot}CO}\\ \|\quad\;\; >\mathrm{O}\\ \mathrm{CH{\cdot}CO}\end{array}$$

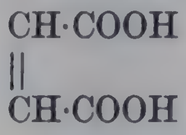
Equiv. wt. 49·01.

Apply the test under "Maleic acid" when a similar result will be obtained.

72° Crotonic acid. $\mathrm{CH_3{\cdot}CH:CH{\cdot}COOH}$. Equiv. wt. 86·05.

To 2 c.c. of Br water add 2 c.c. of the aq. soln. of O.S. and shake,

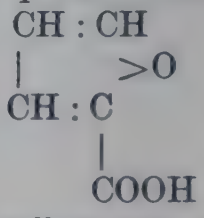
—soln. becomes colourless in about 5 sec.

130° Maleic acid. 

$$\begin{array}{l}\mathrm{CH{\cdot}COOH}\\ \|\\ \mathrm{CH{\cdot}COOH}\end{array}$$

Equiv. wt. 58·02. (Aq. soln. gives no ppt. with aq. $\mathrm{FeCl_3}$.)

Only decolourises Br water on heating. Pour 2 c.c. Br water in each of two t.t.s. To one add an amount of O.S. equivalent to ⅛-in. layer in a t.t. Stand both tubes in boiling water for 2 min. The liquid in the t.t. containing O.S. becomes colourless, while in the other t.t. the brown colour of the Br persists. *p*-Nitrobenzyl ester, m.p. 89°.

133° Furoic (Pyromucic) acid. 

$$\begin{array}{l}\mathrm{CH:CH}\\ |\qquad\;\; >\mathrm{O}\\ \mathrm{CH:C}\\ \qquad\;|\\ \qquad\mathrm{COOH}\end{array}$$

Equiv. wt. 112·0.

(Aq. soln. gives a yellow ppt. with aq. $\mathrm{FeCl_3}$.)

To 2 c.c. Br water add 2 c.c. of the aq. soln. of O.S.,

—soln. immediately becomes colourless.

*p*-Nitrobenzyl ester, m.p. 133° (see page 232).

Section 2.

**α-Hydroxy acids.**

*Preliminary tests.*

(1) To 2 c.c. of the aq. soln. of the free acid or salt add 1 c.c. Denigès soln., heat to boiling and add aq. $\mathrm{KMnO_4}$, drop by drop. If, on the disappearance of the purple colour, a white ppt. is obtained see "Citric acid" (page 73). If no ppt. is obtained apply Test 2.

(2) Place R.G. each of acid or salt and β-naphthol in a dry t.t. and add 5 drops conc. $\mathrm{H_2SO_4}$. Immerse the end of the t.t.

in boiling water for $\frac{1}{2}$ min., shaking the t.t. in order to mix the contents; cool.

If the colour obtained is
(*a*) green, see "Tartaric acid" (page 74).
(*b*) yellow-brown, or deep red-brown, see "Lactic acid" and "Glycollic acid" (page 73).
(*c*) bright yellow with a green fluorescence, see "Malic acid" (page 74).
(*d*) wine-red, see "Mandelic acid" (page 74).

M.p.

18° *dl*-Lactic acid. $CH_3{\cdot}CH(OH){\cdot}COOH$. Usually a syrupy liquid.

(*a*) To a drop of the acid, or $\frac{1}{8}$-in. layer of the salt, in a dry t.t. add 2 c.c. conc. $H_2SO_4$. Warm carefully just until the soln. becomes pale yellow. Cool and add 2 drops of a 5% alcoholic soln. of guaiacol,
—intense red colour (Glycollic acid and its salts give a violet-red colour). Confirm by Test (*b*).

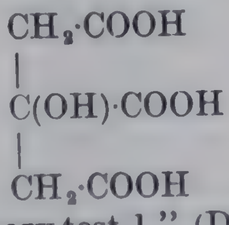
(*b*) To $\frac{1}{8}$-in. layer of acid or salt in a dry t.t. add 5 drops conc. $H_2SO_4$. Warm, revolving the tube, just until the mixture becomes light brown. Cool, dilute to 5 c.c. with water and add solid NaOH until the mixture is strongly alkaline. Heat to boiling and continue boiling for $\frac{1}{2}$ min.,
—disagreeable odour of aldehyde resin.

79° Glycollic acid. $CH_2OH{\cdot}COOH$. Equiv. wt. 76·03. Tends to deliquesce.

(*a*) Apply Test (*a*) under "Lactic acid," when a violet-red colour will be obtained. Confirm by Test (*b*).

(*b*) To $\frac{1}{8}$-in. layer of the acid or salt in a t.t. add an equal bulk of solid $KMnO_4$ and 10 c.c. aq. $Na_2CO_3$.
Heat and shake until the purple colour has entirely disappeared, then filter. To 2 c.c. of the filtrate add 1 c.c. of glacial acetic acid, heat to boiling and add 2–3 drops aq. $CaCl_2$,
—white ppt. (Ca oxalate.)

100° Citric acid (+ $H_2O$).



$$\begin{array}{l} CH_2{\cdot}COOH \\ | \\ C(OH){\cdot}COOH \\ | \\ CH_2{\cdot}COOH \end{array}$$

Equiv. wt. 70·03.

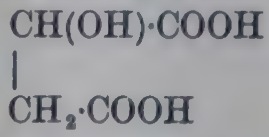
(*a*) See "Preliminary test 1" (Denigès test), page 72.

(*b*) To 3 c.c. of the neutral soln. add 1 c.c. aq. $CaCl_2$, heat to boiling, and continue boiling for 1–2 min.,

M.p.

—heavy crystalline ppt. of Ca citrate. (On applying Test (*d*) under "Tartaric acid" to a soln. of a neutral citrate of an alkali metal, a similar result will be obtained. $NH_4$ citrate, however, merely yields a purple-brown soln.)

100° *l*-Malic acid.



$$\begin{array}{l}\mathrm{CH(OH)\cdot COOH}\\ |\\ \mathrm{CH_2\cdot COOH}\end{array}$$

Equiv. wt. 67·02. Hygroscopic.

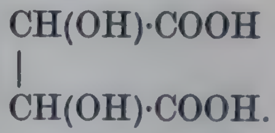
(*a*) See "Preliminary test 2, result (*c*)," page 72.

(*b*) To R.G. each of the acid or salt and resorcinol in a dry t.t. add 2 drops conc. $H_2SO_4$. Warm over a small flame just until effervescence commences. Cool, add a few drops of water, then add aq. NaOH until the mixture is alkaline. Dilute to 100 c.c. with water,
—blue fluorescence.

118° *dl*-Mandelic acid. $C_6H_5\cdot CH(OH)\cdot COOH$. Equiv. wt. 152·1.

To ⅛-in. layer of acid or salt in a t.t. add 5 c.c. of a mixture of equal volumes of aq. $KMnO_4$ and dil. $H_2SO_4$; heat,
—bitter-almond odour of benzaldehyde.

169° *d*-Tartaric acid.



$$\begin{array}{l}\mathrm{CH(OH)\cdot COOH}\\ |\\ \mathrm{CH(OH)\cdot COOH.}\end{array}$$

Equiv. wt. 75·02.

(*a*) See "Preliminary test 2, result (*a*)," page 72.

(*b*) To 2 c.c. of the aq. soln. of acid or salt add R.G. of powdered $FeSO_4$, shake to dissolve and add *one* drop of $H_2O_2$ (20 vol.). Add 2 c.c. aq. NaOH,
—deep violet colour (Fenton's test).

(*c*) To 3 c.c. of the neutral soln. add 1 c.c. aq. $CaCl_2$ and shake vigorously,
—heavy, crystalline ppt. of Ca tartrate (dissolved by adding 1 c.c. glacial acetic acid and boiling).

(*d*) To 5 c.c. aq. $AgNO_3$ add 3–5 drops of the neutral soln., then add dil. $NH_4OH$ drop by drop with shaking until the ppt. is just or almost dissolved. Stand the t.t. in boiling water,
—silver mirror forms.

**B.** *Procedure for the identification of O.S.:—*

Determine the m.p. of the acid (see Note 1 p. 75) and apply the $FeCl_3$ test described on p. 75. Refer, in the appropriate section as indicated by the $FeCl_3$ test, to the list of m.p.s of acids. If one of these m.p.s is identical with, or near to, that of O.S., apply any tests given under that acid. Also, if further evidence of identity appears desirable, prepare and determine the m.p. of one of the derivatives there indicated. (The methods of preparation of the derivatives are given on page 80.)

*$FeCl_3$ test.*

To 2 c.c. of an aq. soln. of a neutral salt of the acid (for preparation see Note 2, page 67) add an equal volume of aq. $FeCl_3$ and note the colour of the soln. or of the ppt. obtained.

| *Result* | *Inference that O.S. is* | *Section in which described* |
|---|---|---|
| Light buff ppt. | a carboxylic derivative of benzene or toluene (see Note 2) | 1 (page 75) |
| Reddish brown ppt. | an aliphatic dibasic acid | |
| Yellow ppt. | cinnamic acid or anisic acid | 3 (page 78) |
| Yellow soln. | benzilic acid | |
| Deep violet colour | salicylic acid, or acetylsalicylic acid (see Note 3) | 4 (page 79) Also see Note 2 |
| Red-brown colour | *m*-hydroxybenzoic acid or *p*-hydroxybenzoic acid | |

NOTES.

(1) If O.S. sublimes, or has not melted when the thermometer registers 230°, proceed as indicated under Section 2 (page 77).

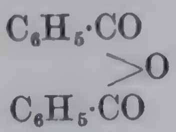
(2) Carboxylic derivatives of benzene or toluene yield the hydrocarbon when heated with soda-lime, while hydroxybenzoic acids yield phenol. Proceed as follows:—Mix a quantity of O.S. which would about half fill the bulb of an ignition tube with three times its bulk of dry soda-lime. Introduce the mixture into the tube and heat. Note if an odour of phenol, or of benzene or toluene, is produced. (A more satisfactory method of detecting the evolved benzene or toluene is given on page 80).

(3) A violet colour is obtained with acetylsalicylic acid in the $FeCl_3$ test owing to hydrolysis to salicylic acid during the preparation of the neutral soln.

**Sparingly soluble acids and anhydrides.**

Section 1.

M.p.
42° Benzoic anhydride.



$$\begin{matrix} C_6H_5{\cdot}CO \\ \quad > O \\ C_6H_5{\cdot}CO \end{matrix}$$

Equiv. wt. 113·0.

(*a*) *Hydrolysis to benzoic acid, m.p.* 121°.

To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. aq. NaOH and heat until a clear soln. is obtained. Cool, acidify with conc. HCl and filter. Wash the solid with cold water, dry, and determine the m.p

M.p.

(*b*) *Preparation of benzanilide, m.p.* 163°.

To ⅛-in. layer of O.S. in a dry t.t. add 1 c.c. aniline. Stand the t.t. in boiling water for 10 min., then remove; add 10 c.c. dil. HCl and shake. Filter, wash the solid with cold water, dry, and determine the m.p.

48° Hydrocinnamic acid. $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$. Equiv. wt. 150·1.

Apply the test under "Phenylacetic acid," when a similar result will be obtained.

Amide, m.p. 105°.

62° Palmitic acid. $CH_3{\cdot}[CH_2]_{14}{\cdot}COOH$. Equiv. wt. 256·3

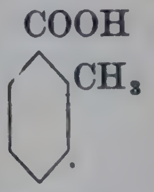
69° Stearic acid. $CH_3{\cdot}[CH_2]_{16}{\cdot}COOH$. ,, ,, 284·3

76° Phenylacetic acid. $C_6H_5{\cdot}CH_2{\cdot}COOH$. Powerful perfume odour. Equiv. wt. 136·1.

In a boiling-tube place the equivalent of ⅛-in. layer in a t.t. of O.S. Add an equal bulk of solid $KMnO_4$ and 5 c.c. dil. $H_2SO_4$; heat to boiling, —bitter-almond odour of benzaldehyde.

Amide, m.p. 157°. Anilide, m.p. 117°. *p*-Nitrobenzyl ester, m.p. 65°.

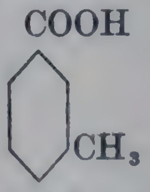
102° *o*-Toluic acid.



Equiv. wt. 136·1.

Amide, m.p. 141°. *p*-Nitrobenzyl ester, m.p. 91°.

110° *m*-Toluic acid.



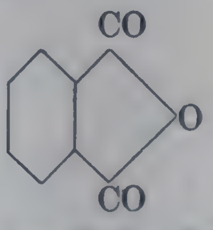
Equiv. wt. 136·1.

Amide, m.p. 94°. *p*-Nitrobenzyl ester, m.p. 87°.

121° Benzoic acid. $C_6H_5{\cdot}COOH$. Equiv. wt. 122·0.

Amide, m.p. 128°. Anilide, m.p. 163°. *p*-Nitrobenzyl ester, m.p. 89°.

131° Phthalic anhydride.



Equiv. wt. 74·02.

(*a*) In a dry t.t. place R.G. of O.S. and twice the bulk of phenol. Add 2 drops conc. $H_2SO_4$ and gently heat just until the mixture is a red-brown colour. Cool, add a few drops of water, then add aq.

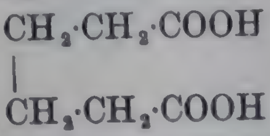
M.p.

NaOH gradually with shaking until the mixture is alkaline,—red colour of phenolphthalein, destroyed by acid.

(*b*) In a dry t.t. place R.G. of O.S. and twice the bulk of resorcinol. Add 2 drops conc. $H_2SO_4$ and gently heat just until the mixture is a red-brown colour. Cool, add a few drops of water, then add aq. NaOH until the mixture is alkaline. Pour 1 c.c. of the alkaline mixture into a t.t. and fill up with water,—yellow-green fluorescence.

*p*-Nitrobenzyl ester, m.p. 155.

150° Adipic acid. Equiv. wt. 73·04.

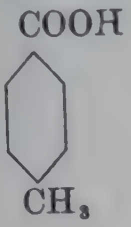


$$\begin{array}{l} CH_2{\cdot}CH_2{\cdot}COOH \\ | \\ CH_2{\cdot}CH_2{\cdot}COOH \end{array}$$

Apply Test (*b*) under "Phthalic anhydride," (page 76) —violet-red colour after rendering the mixture alkaline with NaOH.

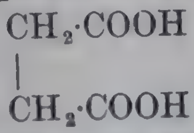
Amide, m.p. 220°. *p*-Nitrobenzyl ester, m.p. 106°.

178° *p*-Toluic acid. Equiv. wt. 136·1.



Amide, m.p. 158°. *p*-Nitrobenzyl ester, m.p. 104°.

185° Succinic acid. Equiv. wt. 59·02.

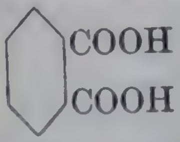


$$\begin{array}{l} CH_2{\cdot}COOH \\ | \\ CH_2{\cdot}COOH \end{array}$$

Apply Test (*b*) under "Phthalic anhydride" (page 76) when a similar result will be obtained.

*p*-Nitrobenzyl ester, m.p. 88°. Anilide, m.p. 226°.

195° –213° Phthalic acid. Equiv. wt. 83·02.



Apply Tests (*a*) and (*b*) under "Phthalic anhydride" (page 76) when similar results will be obtained.

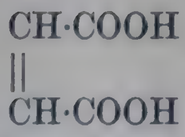
*p*-Nitrobenzyl ester, m.p. 155°.

Section 2.

Determine the equivalent weight of O.S. by Method 1 (page 81) and refer to the list of equivalent weights of acids below. If one of these equivalent weights is identical with, or near to, that of O.S. apply any tests given. Also prepare the derivative there indicated and determine its m.p. The method of preparation of the derivatives is given on page 80

Equiv. wt.

58·02 Fumaric acid.

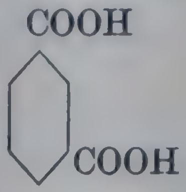


$$\begin{array}{l}CH\cdot COOH\\ \|\\ CH\cdot COOH\end{array}$$

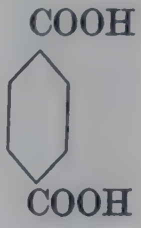
*p*-Nitrobenzyl ester, m.p. 151°.

Apply the test under "Maleic acid" (page 72) when a similar result will be obtained.

83·02 { Isophthalic acid



Terephthalic acid



To ⅛-in. layer of O.S. in a t.t. add 2 c.c. dil. $NH_4OH$ and shake until O.S. has completely dissolved. Add 1 c.c. aq. $BaCl_2$ and shake vigorously. A heavy white ppt. indicates that O.S. is terephthalic acid, the Ba salt of isophthalic acid not being pptd. under these conditions.

Methyl isophthalate, m.p. 64°. Methyl terephthalate, m.p. 140°.

Section 3.

M.p.

133° Cinnamic acid. $C_6H_5\cdot CH:CH\cdot COOH$. Equiv. wt. 148·1.

To 2 c.c. of the neutral soln. add an equal volume of aq. $KMnO_4$ and shake,—purple colour immediately destroyed; brown ppt. and bitter-almond odour of benzaldehyde produced.

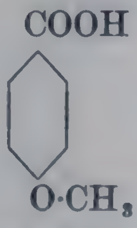
Amide, m.p. 147°. Anilide, m.p. 153°. *p*-Nitrobenzyl ester, m.p. 117°.

150° Benzilic acid. $(C_6H_5)_2C(OH)\cdot COOH$. Equiv. wt. 228·1.

To R.G. of O.S. add a drop of conc. $H_2SO_4$,—intense red colour.

*p*-Nitrobenzyl ester, m.p. 99°.

184° Anisic acid.

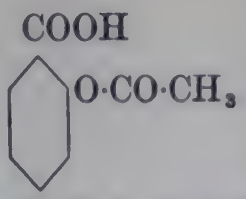


Equiv. wt. 152·1.

Amide, m.p. 162°, Anilide, m.p. 171°. *p*-Nitrobenzyl ester, m.p. 132°.

Section 4.
M.p.

135°. Acetylsalicylic acid (Aspirin).

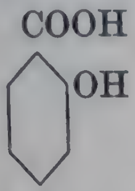


Equiv. wt. 180·1.

(*a*) To 2 c.c. of *cold* water add R.G. of O.S. and shake, then add one drop of aq. $FeCl_3$,—no violet colour (distinction from salicylic acid).

(*b*) Apply Tests (*b*) and (*c*) under " Salicylic acid " when similar results will be obtained.

158° Salicylic acid.



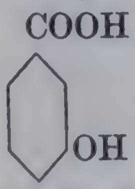
Equiv. wt. 138·0.

(*a*) Apply Test (*a*) under " Acetylsalicylic acid " when a violet colour will be obtained.

(*b*) To $\frac{1}{8}$-in. layer of O.S. (acid or salt) in a t.t. add 1 c.c. conc. $HNO_3$. Stand the t.t. in boiling water for 5 min. then remove and fill up with water. To 2 c.c. of the yellow soln. (picric acid) add aq. NaOH until alkaline, then add 2 drops $NH_4$ sulphide and stand the t.t. in boiling water for 1 min.,—deep red colour due to an alkali salt of picramic acid.

(*c*) To $\frac{1}{8}$-in. layer of O.S. (acid or salt) in a dry t.t. add 10 drops each of methyl alcohol and conc. $H_2SO_4$ and heat gently. Cool and pour into 5 c.c. water contained in a dish,—odour of " Oil of wintergreen " (methyl salicylate).

200° *m*-Hydroxybenzoic acid.

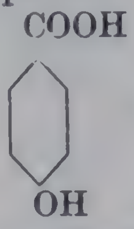


Equiv. wt. 138·0.

Apply Test (*b*) under " Salicylic acid," when a similar result will be obtained.

Acetyl derivative, m.p. 131°.

213° *p*-Hydroxybenzoic acid.



Equiv. wt. 138·0.

Apply Test (*b*) under " Salicylic acid," when a similar result will be obtained.

Acetyl derivative, m.p. 187.

*Preparation of benzene or toluene from their carboxylic derivatives.* To ¼-in. layer of O.S. in a dry t.t. add 1-in. layer of dry soda-lime, pour into a mortar and grind together, then return the mixture to the t.t. Fit the t.t. with a cork and bent delivery tube (with the long limb about 7 in.), place the t.t. across a tripod and arrange a second dry t.t. so that the end of the delivery tube reaches to the bottom of it. Heat the mixture fairly strongly but not so strongly as to soften and spoil the t.t. Finally heat the whole t.t. and the upper part of the delivery tube so as to drive any liquid present into the receiver. To the distillate add 3 drops each of conc. $HNO_3$ and conc. $H_2SO_4$, warm slightly, dilute to 5 c.c. with water and pour into a dish. A bitter-almond odour of nitrobenzene or the somewhat similar odour of a mono-nitrotoluene indicates that the distillate is benzene or toluene.

## METHODS OF PREPARATION OF THE DERIVATIVES INDICATED UNDER THE ACIDS IN THE FOREGOING LISTS

(See sections on "Crystallisation" and "Drying of substances," pages 16–21.)

### Amides, anilides, and methyl esters.

(These preparations should be carried out in a fume cupboard. Also, when adding a reagent to the crude acid chloride, the t.t. containing the former should be held at arm's length.)

First convert the acid into its chloride as follows :—In a porcelain dish place ½ g. of the acid and 2 g. $PCl_5$. Grind the substances together by means of a pestle until the mixture becomes liquid. (If O.S. is assumed to be isophthalic acid or terephthalic acid use. twice the amount of $PCl_5$ and assist the liquefaction by warming.)

### Preparation of the amide.

To the crude acid chloride add 10 c.c. conc. $NH_4OH$. When the vigorous reaction has ceased, stir, cool and filter. Wash the solid with cold water, crystallise from water, dry, and determine the m.p.

### Preparation of the anilide.

Dissolve the crude acid chloride in 5 c.c. acetone and pour the soln. into a 100-c.c. flask. Add 1 c.c. freshly distilled aniline and cool. Add 30 c.c. aq. NaOH, cork the flask and shake for 10 min. Filter, wash the solid with cold water, crystallise from alcohol, dry, and determine the m.p.

### Preparation of the methyl ester of isophthalic acid, or terephthalic acid.

To the crude acid chloride add 10 c.c. methyl alcohol and stir. Allow to stand 10 min., then add 10 c.c. water. (If O.S. is terephthalic acid the methyl ester will separate as a bulky ppt. after standing for a few seconds.) Filter, wash the solid with cold water, crystallise from methyl alcohol in the case of the terephthalate, or from aqueous methyl alcohol in the case of the isophthalate. Dry the solid and determine the m.p.

**Acetyl derivatives of *m*-hydroxybenzoic acid and *p*-hydroxybenzoic acid.**

To ¼-in. layer of the acid in a t.t. add 2 c.c. acetic anhydride and one drop conc. $H_2SO_4$; heat just to boiling. Cool, pour into 5 c.c. water and heat until the lower layer has completely dissolved. (If the lower layer almost immediately solidifies, as will be the case when *p*-hydroxybenzoic acid is acetylated, no further heating is necessary.) Cool and shake, filter, wash the solid with cold water, dry, and determine the m.p.

**_p_-Nitrobenzyl esters.** See page 232.

## DETERMINATION OF THE EQUIVALENT WEIGHT OF AN ACID OR ANHYDRIDE

(A list of equivalent weights is given on page 86.)

*Method 1.*

Titration with $\frac{N}{10}$ NaOH, with phenolphthalein as indicator.

(*a*) Standardise an approximately $\frac{N}{10}$ NaOH soln. (4 g. NaOH per litre) as follows :—

Weigh accurately a watch-glass or weighing bottle, add about 0·2 g. of pure succinic acid (equiv. wt. = 59·02) and weigh again. Wash the acid with distilled water into a beaker (250 c.c. or larger) or through a sufficiently large funnel into a 250-c.c. conical flask.

Add 2 or 3 drops of phenolphthalein soln. and titrate with the NaOH soln. until a red colour, which persists for a minute, is obtained.

(0·2000 g. of succinic acid requires 33·9 c.c. of exactly $\frac{N}{10}$ NaOH.)

$$\text{Factor of alkali} = \frac{\text{wt. of acid}}{\text{vol. of alkali}} \times \frac{1{,}000}{\text{equiv. wt. of acid}}$$

Other pure organic acids may be used, e.g. oxalic (hydrated, equiv. wt. = 63·02), tartaric (equiv. wt. = 75·02) or citric (hydrated, equiv. wt. = 70·03).

(*b*) Weigh out 0·2–0·6 g. of the acid or anhydride whose equiv. wt. is to be determined. If readily soluble in cold water wash it into the beaker or flask with distilled water; if sparingly soluble in cold water use neutralised alcohol (prepared by adding phenolphthalein to alcohol, then adding $\frac{N}{10}$ NaOH drop by drop until a faint red colour persists after shaking round. A small wash bottle should be kept specially for the alcohol).

It is advisable to weigh out an oily liquid or a wax-like solid directly into a 175 c.c. flask and then to add about 25 c.c. of neutralised alcohol.

Add phenolphthalein soln. and titrate with the standardised $\frac{N}{10}$ NaOH until a permanent red colour is obtained.

Equiv. wt. of an acid or anhydride = wt. of acid or anhydride neutralised by 1,000 c.c. N. NaOH.

**Example.**

35·5 × 0·102 c.c. N. NaOH neutralised 0·2284 g. of acid (oxalic).

$$\text{1,000 c.c. N. NaOH} \quad ,, \quad \frac{0{\cdot}2284 \times 1{,}000}{35{\cdot}5 \times 0{\cdot}102} \quad ,,$$

$$= 63{\cdot}08 \text{ g.}$$

Therefore equiv. wt. of acid = 63·1. (Theory = 63·02.)

Below are given results obtained with other commercially pure acids. From the data the approximate weights of acids suitable for titration with $\frac{N}{10}$ NaOH will be seen. The acids marked with an asterisk were dissolved in neutralised alcohol, the remainder in water.

| *Acid* | *Wt.* | *Vol. of 0·1020.N NaOH required* | *Equiv. Wt.* | |
|---|---|---|---|---|
| | | | *Found* | *Calculated from formula* |
| Tartaric . . . . . | 0·3040 g. | 39·7 c.c. | 75·1 | 75·02 |
| Citric . . . . . . | 0·3026 g. | 42·3 c.c. | 70·1 | 70·03 |
| Benzoic * . . . . . | 0·3994 g. | 32·1 c.c. | 122·0 | 122·0 |
| Salicylic * . . . . . | 0·5034 g. | 35·8 c.c. | 137·8 | 138·0 |
| Phthalic . . . . . | 0·3034 g. | 35·75 c.c. | 83·2 | 83·02 |
| Cinnamic * . . . . | 0·5016 g. | 33·2 c.c. | 148·1 | 148·1 |
| Phenylacetic * . . . | 0·5002 g. | 36·0 c.c. | 136·2 | 136·1 |
| Anthranilic . . . . | 0·5012 g. | 35·8 c.c. | 137·3 | 137·1 |
| Hippuric * . . . . . | 0·7000 g. | 38·2 c.c. | 179·7 | 179·1 |
| Sulphanilic . . . . . | 0·6026 g. | 34·15 c.c. | 173·0 | 173·1 |
| Metanilic . . . . . | 0·6030 g. | 34·05 c.c. | 173·6 | 173·1 |

In the case of acid anhydrides and acids which are practically insoluble in water and alcohol (e.g. terephthalic acid) the substance must be boiled with a definite volume of NaOH (in considerable excess of that required for neutralisation) and the excess of alkali determined by titration with standard acid.

*Method 2.*

**Analysis of the Ag salt.**

This method depends on the fact that Ag salts of organic acids (containing only C, H, and O) leave on ignition a residue of pure Ag. Ag salts are usually normal salts, are often sparingly soluble, and crystallise without water of crystallisation, hence are particularly suitable for equivalent weight determinations. Some, however (e.g. Ag oxalate), explode on heating.

*Procedure :—*

(In all the following operations the Ag salt should be protected as much as possible from the action of light.)

Dissolve about 1 g. of the acid in dil. $NH_4OH$ (the soln. must be alkaline), boil until the soln. is neutral; cool. (If the $NH_4$ salt of the acid crystallises out, as in the case of $NH_4$ cinnamate, use a warm soln.) Add conc. aq. $AgNO_3$ until no more ppt. is formed, filter by suction, wash the Ag salt three times with cold distilled water, draining as dry as possible each time, and allow to dry in a desiccator in the dark. (If speed is essential, after the last washing with water, wash similarly twice with alcohol and then twice with ether, and dry in a steam oven.) Weigh out accurately in a crucible (which has previously been heated to redness, allowed to cool in a desiccator and weighed) about 0·5 g. of the dry Ag salt.

In order to prevent spirting the salt should be heated by one of the following methods.

(*a*) Place the crucible in an inclined position on a pipe-clay triangle supported on a tripod. Place a small flame under the lower rim of the crucible so that the salt is heated first by conduction down the side of the crucible. Gradually move the flame along the crucible until it is directly underneath the salt. Finally heat to redness with a large flame, cool in a desiccator and weigh. Repeat heating, cooling, and weighing until the weight is constant.

(*b*) Place the crucible on a pipe-clay triangle supported on the chimney of an Argand burner. At the beginning of the heating reduce the flame to the smallest blue ring. As decomposition proceeds, gradually increase the size of the flame. Finally heat the crucible to redness over a large Bunsen flame, etc. as in (*a*).

Calculate the weight of Ag salt equivalent to 107·9 g. of Ag. Subtract from this 107·9 g. for the gram equiv. wt. of Ag, and add 1 g. for the H which the Ag has replaced in the acid.

Results differing from the theoretical figure by not more than 0·2% should be obtained.

EXAMPLES.

(1) 0·7280 g. of Ag cinnamate yielded 0·3080 g. of Ag.

i.e. 0·308 g. of Ag is contained in 0·728 g. of Ag salt.

$$107{\cdot}9\text{ g.}\quad\text{,,}\quad\text{are}\quad\text{,,}\quad\text{,,}\quad \frac{0{\cdot}728}{0{\cdot}308} \times \frac{107{\cdot}9}{1}\text{ g. of Ag salt}$$

$$= 255{\cdot}1\text{ g.}$$

Equiv. wt. of acid = 255·1 − 107·9 + 1 = 148·2.

,, ,, ,, calculated from formula = 148·1.

(2) 0·5220 g. of Ag. benzoate gave 0·2460 g. of Ag.

Equiv. wt. of benzoic acid = 122·2. (Theory 122·0.)

*Method 3.*

**Analysis of a Ba or Ca salt.**

If the addition of conc. aq. $BaCl_2$ or $CaCl_2$ to a conc. neutral soln. of the $NH_4$ salt of the acid yields a ppt., the Ba or Ca salt obtained (after filtering off, washing, and drying), may be used for the determination of the equiv. wt. of the acid.

The disadvantage of the method is that the salt may contain water of crystallisation, and it is therefore necessary before use to heat it in an air oven to about 130° until constant in weight.

The method employed is to heat a weighed quantity of the Ba or Ca salt with $H_2SO_4$ and to weigh the residue of $BaSO_4$ or $CaSO_4$. From the weight of sulphate obtained the weight of Ba or Ca in the original salt is calculated.

$$\text{Thus } \frac{137{\cdot}4}{233{\cdot}4} \times \text{wt. of } BaSO_4 = \text{wt. of Ba in the original salt.}$$

$$\frac{40{\cdot}08}{136{\cdot}1} \times \text{wt. of } CaSO_4 = \text{,,}\quad\text{,, Ca}\quad\text{,,}\quad\text{,,}\quad\text{,,}$$

Next the weight of salt equivalent to 68·68 g. of Ba (or 20·04 g. of Ca) is calculated. From this is subtracted 68·68 g., for the gram equiv. wt. of Ba (or 20·04 g. for the gram equiv. wt. of Ca), and 1 g. is added for the H which the Ba (or Ca) has replaced; the result is the gram equiv. wt. of the acid.

*Procedure :—*

For the heating it is convenient to employ a retort stand fitted with a ring upon which rests a pipe-clay triangle. (An alternative method is to use an Argand burner in the manner described in method 2 (*b*)). Heat a crucible (preferably a deep silica one) to redness on a triangle, cool in a desiccator and weigh.

Place a layer of the Ba or Ca salt ($\frac{1}{16}$ in. to $\frac{1}{8}$ in. deep) in the bottom of the crucible and weigh again. Just moisten the whole of the salt with 50% $H_2SO_4$, using a dropping tube. Place the crucible on a pipe-clay triangle supported on a retort ring, and adjust the height on a retort stand so that when a Bunsen is placed underneath, the bottom of the crucible will be about 4 in. above the top of the burner.

Heat with a very small flame and gradually raise the temperature of the crucible by bringing the ring nearer to the flame. (The very gradual heating is necessary in order to prevent excessive frothing and the creeping of the mixture too far up the sides of the crucible.) When the contents are dry, place the crucible in an inclined position on the triangle, and heat by placing a small flame under the lower rim. Gradually move the flame along until it is directly under the bottom of the crucible. Finally heat to redness in a large flame until any carbon present has burnt away and the residue is white. (The removal of carbon is facilitated by using a large Méker burner and moving the crucible about.)

Allow to cool, moisten with 50% $H_2SO_4$ and drive off the excess acid in the same manner as before, finally heat to redness, cool in a desiccator and weigh.

Repeat heating, for periods of 10 min., until the weight is constant. The percentage of Na, K, Sr, and Pb, as well as Ba and Ca in salts may be similarly estimated.

The student should, for practice, carry out duplicate estimations of the percentage of metal in several commercially pure salts without removing any water of crystallisation present.

Below are shown duplicate results obtained with commercially pure salts, together with the percentage of metal calculated from the formula :

(C = 12·00, H = 1·008, O = 16·00, Ba = 137·36, Ca = 40·08, Na = 23·00.)

| | *Calculated* | *Found* | *Difference between results* |
|---|---|---|---|
| Calcium formate, $(CHO_2)_2Ca$ | % Ca = 30·82 | 30·77<br>30·69 | 0·26% |
| ,, lactate, $(C_3H_5O_3)_2Ca,5H_2O$ | ,, = 13·00 | 13·23<br>13·21 | 0·15% |
| ,, tartrate, $C_4H_4O_6Ca,4H_2O$ | ,, = 15·40 | 15·43<br>15·37 | 0·39% |
| ,, citrate, $(C_6H_5O_7)_2Ca_3,4H_2O$ | ,, = 21·07 | 21·92<br>21·88 | 0·18% |
| ,, benzoate, $(C_7H_5O_2)_2Ca,2H_2O$ | ,, = 12·60 | 12·49<br>12·47 | 0·16% |
| Barium acetate, $(C_2H_3O_2)_2Ba,H_2O$ | % Ba = 50·25 | 50·30<br>50·30 | |
| Sodium benzoate, $C_7H_5O_2Na$ | % Na = 15·97 | 15·72<br>15·70 | 0·13% |

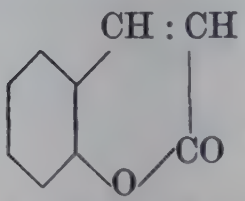
*Equivalent weights of acids and anhydrides*

(Calculated—C = 12·00, H = 1·008, O = 16·00)

| | | | |
|---|---|---|---|
| 46·02. | Formic acid. | 86·05. | Crotonic acids. |
| 49·01. | Maleic anhydride. | 88·06. | Butyric acids. |
| 50·02. | Succinic anhydride. | 90·05. | Lactic acid. |
| 51·02. | Acetic anhydride. | 102·1. | Valeric acids. |
| 52·02. | Malonic acid. | 112·0. | Furoic acid. |
| 58·02. | Maleic acid. | 113·0. | Benzoic anhydride. |
| 58·02. | Fumaric acid. | 122·0. | Benzoic acid. |
| 59·02. | Succinic acid. | 136·1. | Phenylacetic acid. |
| 60·03. | Acetic acid. | 136·1. | Toluic acids. |
| 63·02. | Oxalic acid ($2H_2O$). | 138·0. | Hydroxybenzoic acids. |
| 66·03. | Glutaric acid. | 148·1. | Cinnamic acid. |
| 67·02. | Malic acid. | 150·1. | Hydrocinnamic acid. |
| 70·03. | Citric acid ($H_2O$). | 152·1. | Mandelic acid. |
| 73·04. | Adipic acid. | 152·1. | Anisic acid. |
| 74·02. | Phthalic anhydride. | 180·1. | Acetylsalicyclic acid. |
| 74·05. | Propionic acid. | 228·1. | Benzilic acid. |
| 75·02. | Tartaric acid. | 256·3. | Palmitic acid. |
| 76·03. | Glycollic acid. | 282·3. | Oleic acid. |
| 83·02. | Phthalic acids. | 284·3. | Stearic acid. |

## LACTONES AND PEROXIDES

M.p.
67° Coumarin.



Fragrant odour. Sparingly soluble in water. Dissolves in hot aq. NaOH yielding a yellow soln. which on acidifying with HCl gives a white ppt. of coumaric acid.

*Preparation of $HgCl_2$ compound, m.p. 164°.*

To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. alcohol, warm until the solid has dissolved, then cool. Add a cold soln. of $\frac{1}{8}$-in. layer in a t.t. of $HgCl_2$ in 5 c.c. of 25% alcohol; shake. Filter off the ppt. of fine needles which separates, wash with cold water, dry, and determine the m.p.

103° Benzoyl peroxide. $C_6H_5{\cdot}CO{\cdot}O{\cdot}O{\cdot}CO{\cdot}C_6H_5$.

Faint sweet odour. Insoluble in water. Explodes on heating.

*Preparation of benzoic acid, m.p. 121°.*

To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 3 c.c. of 20% aq.

KOH and boil until all the solid has dissolved. (An effervescence will be observed, due to the evolution of oxygen.) Acidify the soln. with conc. HCl, cool and filter. Wash the solid with cold water, dry, and determine the m.p.

## SALTS OF CARBOXYLIC ACIDS

### Identification of the acid radical.

If only Na or K is present see "Procedure I"; if any other metal is present see "Procedure II" (page 89).

*Procedure I :—*

If O.S.

(*a*) does not yield an acid aq. soln., to ⅛-in. layer of O.S. in a t.t. add 5 c.c. distilled water and shake. If O.S. does not dissolve, heat until solution is complete, then cool.

If (i) a clear soln. is obtained, dilute to 10 c.c. with distilled water and proceed as under **A.**

(ii) a lather was produced during the dissolving of O.S. and a white gelatinous mass was obtained on cooling the soln. a salt of palmitic, stearic, or oleic acid is indicated. Proceed as under **B** (page 89).

(*b*) yields an acid aq. soln., to ⅛-in. layer of O.S. in a t.t. add sufficient dil. $NH_4OH$ to yield an alkaline soln. and dilute to 10 c.c. with distilled water. Pour the soln. into a dish and boil until a piece of red litmus paper momentarily immersed in the soln. is just no longer turned blue, keeping the volume between 5 c.c. and 10 c.c. by the addition, when necessary, of distilled water. Cool, make up the volume to 10 c.c. with distilled water and proceed as under **A.**

A.

(*a*) To 2 c.c. of the neutral soln. add ½ the volume of glacial acetic acid. If a ppt. is obtained (indicating the liberation of a sparingly soluble acid) apply Test (*b*); if no ppt. is produced, heat to boiling and add 2–3 drops aq. $CaCl_2$.

An immediate white ppt. indicates an oxalate; apply the test under (ii), page 70.

If no ppt. is obtained apply Test (*b*).

(*b*) To 2 c.c. of the neutral soln. (and also to an equal volume of water as a blank test) add 3 drops aq. $FeCl_3$, observe the effect and then add an equal volume of aq. $FeCl_3$.

| *With equal volume aq.* $FeCl_3$ | *With 3 drops aq.* $FeCl_3$ | *Inference and procedure* |
|---|---|---|
| Wine-red colour (viewed through depth of liquid). No ppt. Reddish-brown ppt. on boiling. | Reddish-yellow colour. No ppt. | Formate, acetate, or propionate. Apply Test (*b*) under corresponding acids (page 68). |
| Deep yellow colour. No ppt. | Strong yellow colour. No ppt. | Salt of α-hydroxy acid. Proceed as indicated under "α-hydroxy acids," (page 72). |
| Deep violet colour. | Violet or red colour. | Salt of a phenolic acid. Proceed as under (*c*). |
| Yellow ppt. | Usually similar, less dense ppt. | Cinnamate or anisate Proceed as under (*c*). |
| Light buff ppt. | | Salt of a simple saturated aromatic acid. Proceed as under (*c*). |
| Reddish-brown ppt. | | Salt of an aliphatic acid. Proceed as under (*c*). |

If results, other than those described above, are obtained, proceed as under (*c*).

(*c*) Prepare a soln. of O.S. by dissolving about 5 times the amount of O.S. previously taken in the minimum amount of water. Add 1 c.c. conc. HCl; if no immediate ppt., cool and shake vigorously.

If (1) a ppt. is obtained, filter, wash the solid with cold water (see note), dry and proceed as indicated under **B** (page 74).

NOTE.

If a ppt. was only obtained after cooling and shaking, as would usually be the case with a salt of succinic or adipic acid, the washing must be carried out very carefully.

(2) an odour of rancid butter, or other unpleasant odour; or an oil is obtained, extract with ether (see page 21). If no oil is present first saturate the soln. with anhydrous $CaCl_2$. Dry the ethereal soln. with anhydrous $CaCl_2$ and distil off the ether. Determine the b.p. of the residue and see list of b.ps. (pages 68, 69).

(3) neither of the results described under (1) and (2) is obtained, determine the equivalent weight of the

corresponding acid by method 2 (page 83), or method 3 (page 84) and refer to the list of equivalent weights of acids (page 86). If one of these equivalent weights is identical with, or near to, that of the acid of which O.S. is the salt, apply any tests given under that acid (pages 71–72).

**B.** *Procedure for the identification of an alkali salt of palmitic, stearic, or oleic acid:—*

Dissolve about 1 g. of O.S. in 20 c.c. hot water and acidify the soln. with conc. HCl. If the liberated acid is a solid, heat until it has melted.* Pour the hot mixture into a small separating funnel (containing about 10 c.c. water to prevent cracking); cool. Extract with ether (see page 21), dry the ethereal soln. with anhydrous $CaCl_2$, distil off the ether and cool the residue.

If the residue is

(*a*) a liquid, see "Oleic acid" (page 69).

(*b*) a solid, see "Palmitic acid," and "Stearic acid" (page 76).

*Procedure II:—*

Pour 20 c.c. distilled water into a dish, heat to boiling and add the equivalent of $\frac{1}{8}$-in. layer in a t.t. of anhydrous $Na_2CO_3$ and an equal bulk of O.S. Continue boiling gently with stirring for 5 min. Test the soln. with red litmus paper; if not alkaline, add solid $Na_2CO_3$ gradually with stirring until an alkaline reaction is obtained. Filter.*

Pour the clear filtrate (see note below) into a dish. If the volume is considerably more than 5 c.c. boil down to about this volume. Remove the flame and add dil. $HNO_3$ with stirring until a piece of blue litmus paper momentarily immersed in the soln. is just turned definitely red. Add dil. $NH_4OH$ with stirring until any solid which has been pptd. is completely dissolved and the soln. is just alkaline. Boil until a piece of red litmus paper momentarily immersed in the soln. is just no longer turned blue, keeping the volume between 5 c.c. and 10 c.c. by the addition, when necessary, of distilled water.

Cool, make up the volume to 10 c.c. with distilled water and apply the tests under **A** (page 87). For Test (*c*) proceed as indicated above under "Procedure II" as far as the asterisk, but using about 5 times the amount of $Na_2CO_3$ and of O.S. (see note). Cool the filtrate, pour into a small beaker, add conc. HCl with stirring until the liquid is acid, then proceed as indicated in Test (*c*) after the acidification with HCl.

NOTE.

If the filtrate is not perfectly clear, re-filter until this condition is attained. If, however, the filtrate consists of a white emulsion, which yields a gelatinous mass on cooling, or a thick lather on shaking vigorously, boil about 1 g. of O.S. with 20 c.c. dil. $HNO_3$ until the solid has disappeared, leaving an oily layer on the surface of the acid, then proceed as under **B** (page 89) commencing at the asterisk.

## *CARBOHYDRATES*

### I. Carbohydrates readily soluble in water, detected by Molisch's test. (Test 3, page 30.)

NOTES.

(1) The aq. soln. referred to in the tests is that which has been employed for Molisch's test, i.e. $\frac{1}{8}$-in. layer of O.S. in a t.t. dissolved in 10 c.c. water.

(2) The m.p.s are of little value for identification purposes since carbohydrates seldom melt sharply owing to the fact that fusion is nearly always preceded by slight decomposition. Their specific rotations are the most important physical constants.

(For method of determination and values a suitable text-book should be consulted.)

*Procedure for the identification of O.S.:—*

To 2 c.c. Fehling's soln. (equal volumes of No. 1 and No. 2) add 1 c.c. of the aq. soln. of O.S. and stand the t.t. in boiling water for *1 min.*

If (*a*) the whole mixture becomes red, due to suspended $Cu_2O$, proceed as under **A.**

(*b*) the mixture remains blue, and is either clear, or only a very slight yellowish turbidity is present, proceed as under **B** (page 92).

A. Apply the following test :—

To 2 c.c. of Barfoed's soln. add an equal volume of the aq. soln. of O.S. and stand the t.t. in briskly boiling water for *2 min.*

If a red ppt. of $Cu_2O$ is observed in the blue soln., or on the sides of the tube just above the liquid, apply the tests (given below) for glucose, fructose, and galactose; if no red ppt. is obtained, apply the tests for lactose and maltose (page 92).

*Tests for glucose, fructose, and galactose.*

(*a*) To 5 c.c. of the aq. soln. of O.S. add 10 drops of glacial acetic acid and 5 drops of phenylhydrazine; shake. Loosely cork the t.t. and stand it in boiling water for 10 min., periodically shaking. If a bulky yellow ppt. is produced, apply Test (*b*); if no such ppt. is obtained, apply Test (*d*).

(The yellow ppt. is an osazone, the same one being formed from both glucose and fructose. The osazone of galactose does not separate under the above conditions.)

(*b*) To 2 c.c. of the aq. soln. of O.S. add the equivalent of $\frac{1}{8}$-in. layer in a t.t. of solid lead acetate, heat to boiling and add 5 c.c. dil. $NH_4OH$. Heat the mixture again to boiling and continue boiling for about 1 min. A salmon-pink or rose-pink colour indicates that O.S. is Glucose (Dextrose, Grape-sugar) $CH_2OH{\cdot}[CH(OH)]_4{\cdot}CHO$, m.p. 146° (anhydrous). 80°–90° (1 mol. $H_2O$).

If a buff colour is obtained proceed with Test (*c*).

(*c*) To 2 c.c. of the aq. soln. of O.S. add an equal volume of conc. HCl and R.G. of resorcinol. Stand the t.t. in boiling water for *2 min.* A deep wine-red colour, usually followed by a ppt. which dissolves in alcohol yielding a deep wine-red soln., indicates that O.S. is Fructose (Levulose, Fruit sugar) $CH_2OH{\cdot}[CH(OH)]_3{\cdot}CO{\cdot}CH_2OH$, m.p. 95°–105°. See also page 94.

(*d*) Place $\frac{1}{2}$ g. of O.S. in a dry t.t. Add $1\frac{1}{2}$ c.c. $HNO_3$ (conc. $HNO_3 + \frac{1}{2}$ its volume of water). Stand the t.t. in boiling water until effervescence commences and red fumes are evolved, then transfer the tube to water which has been heated to 70°. Allow to stand for 15 min., keeping the water at 65°–70°.

A white, sandy ppt. (mucic acid) indicates that O.S. is Galactose, $CH_2OH{\cdot}[CH(OH)]_4{\cdot}CHO$, m.p. 168° (anhydrous). 119° (1 mol. $H_2O$).

*Tests for lactose and maltose.*

(*a*) To 2 c.c. of the aq. soln. of O.S. add the equivalent of a $\frac{1}{4}$-in. layer in a t.t. of solid lead acetate, heat to boiling and add twice the volume of dil. $NH_4OH$ (with lactose a dense white ppt. is obtained ; with maltose only a slight ppt. is formed). Heat to boiling and continue boiling gently for *1 min.*

A salmon-pink colour indicates that O.S. is Lactose (Maltose gives only an orange-yellow colour). Confirm by Test (*b*).

(*b*) Proceed exactly as described in Test (*d*), page 92.

Finally remove the t.t. from the hot water, cool and scrape the inside of the tube in contact with the liquid with a glass rod for 3 min.

A white, sandy ppt. (mucic acid) indicates that O.S. is Lactose (Milk sugar) $C_{12}H_{22}O_{11}$, m.p. 203° decomp. (The amount of ppt. will increase considerably on standing.)

Maltose $C_{12}H_{22}O_{11}$ (Malt sugar, m.p. 100° decomp.) does not yield a ppt.

**B.** Apply the following tests for sucrose and inulin :—

(*a*) To 2 c.c. of the aq. soln. of O.S. add an equal volume of conc. HCl and R.G. of resorcinol. Stand the t.t. in boiling water for *2 min.*

A deep wine-red colour, usually followed by a ppt. which dissolves in alcohol to a deep wine-red soln. (due to fructose, formed by hydrolysis), indicates that O.S. is Sucrose (Cane sugar) $C_{12}H_{22}O_{11}$, m.p. 160°, or Inulin $(C_6H_{10}O_5)n$ (decomposes on heating). Distinguish by Tests (*b*) and (*c*).

(*b*) To ⅛-in. layer of O.S. in a t.t. add 2 c.c. aq. NaOH, heat to boiling and continue boiling for ½ min.

A deep yellow soln. indicates that O.S. is Inulin. Sucrose yields an almost colourless soln.

(*c*) In a 100-c.c. flask place the equivalent of a ¼-in. layer in a t.t. of O.S. and add 50 c.c. dil. HCl (1 c.c. conc. HCl diluted to 100 c.c. with water).

Heat to boiling, continue boiling gently for 10 min., then cool.

Add a drop or two of phenolphthalein soln. and just sufficient aq. NaOH to give a permanent red colour. Add dil. acetic acid, drop by drop, until the soln. is just colourless.

The soln. obtained from either sucrose or inulin will reduce Fehling's soln. and also Barfoed's soln. (See under **A**, page 91).

The soln. obtained from sucrose, but not that from inulin, will give the test for glucose (*b*) (page 92) if double the amount of lead acetate is employed.

**II. Starch** $(C_6H_{10}O_5)n$.

This carbohydrate will have been indicated by the blue colour obtained on the addition of iodine to its aqueous solution (Test (*b*) under "No metal present," page 28).

Confirm by the following tests :—

(*a*) Apply Molisch's test (Test 3, page 30). Use a soln. obtained by boiling R.G. of O.S. with 2 c.c. water and cooling.

A positive result will be obtained.

(*b*) Heat 50 c.c. water, contained in a beaker, to boiling. Shake ⅛-in. layer of O.S. in a t.t. with 5 c.c. water, pour the mixture into the beaker, boil for 1 min., then cool. Apply the following tests :—

(1) Add 5 c.c. of the aq. soln. of O.S. to 50 c.c. water to which one drop of iodine soln. has been added,
—deep blue colour.
Heat 5 c.c. of the blue soln. in a t.t.,—blue colour disappears and reappears on cooling.

(2) Add 2 c.c. of the aq. soln. of O.S. to 2 c.c. Fehling's soln. (equal volumes of No. 1 and No. 2), heat to boiling and continue boiling for ½ min.,—no reduction, i.e. no red ppt. of $Cu_2O$.

(*c*) Shake ¼-in. layer of O.S. in a t.t. with 5 c.c. cold water.

Pour the mixture into 50 c.c. of boiling dil. HCl (5 c.c. conc. HCl diluted to 100 c.c. with water), boil gently for 10 min., then cool (a clear soln. will be obtained with potato starch, whereas rice starch yields a slightly opalescent soln.). Add a drop or two of phenolphthalein soln. and just sufficient aq. NaOH to give a permanent red colour. Add dil. acetic acid, drop by drop, until the soln. is just colourless.

Repeat both the tests under (*b*) with this soln.

(1) No blue colour will be obtained with the iodine soln.

(2) Fehling's soln. will be reduced, i.e. the whole mixture will become red, due to suspended $Cu_2O$.

The above results are due to the fact that by boiling with the mineral acid the starch has been completely hydrolysed to glucose.

## GLUCOSIDES

The only glucoside likely to be encountered is Salicin, $C_{13}H_{18}O_7$, m.p. 201°.

This substance will have been indicated in Test 3 (page 30) by the intense red colour given with cold conc. $H_2SO_4$.

*Confirmatory test.*

Boil the equivalent of ⅛-in. layer in a t.t. of O.S. with 25 c.c. dil. $H_2SO_4$ (1½ c.c. conc. $H_2SO_4$ diluted to 100 c.c. with water) in a 100-c.c. flask.

In about 10 min. a white ppt. will appear (saliretan, a condensation product of salicyl alcohol). Pour 1 c.c. of the mixture into a t.t., add aq. NaOH until the mixture is alkaline, then add an equal volume of Fehling's soln. (equal volumes of No. 1 and No. 2) and boil for ½ min.,—whole mixture becomes red, due to suspended $Cu_2O$. (The reduction is caused by glucose formed by hydrolysis. An aq. soln. of salicin will not reduce Fehling's soln.)

To the mixture in the flask add the equivalent of ⅛-in. layer in a t.t. of solid $K_2Cr_2O_7$ and 10 c.c. dil. $H_2SO_4$. Connect the flask to a water condenser and distil until 4–5 c.c. is present in the receiver. The distillate will possess the characteristic odour of salicylaldehyde. Apply the following tests for this aldehyde :—

(*a*) To half the distillate add one drop of aq. $FeCl_3$,—violet-red colour.

(*b*) To the other half of the distillate add one drop of aq. NaOH, —yellow colour.

*Further distinction between glucose and fructose :*

In a t.t. place 2. R.G. of O.S. and R.G. of sodium selenite (or $SeO_2$). Add 2 c.c. of dil. HCl and stand the t.t. in boiling water for 2 min. A finely-divided red ppt. of selenium is obtained with fructose, whereas with glucose the soln. remains clear and colourless.

# *COLOURED SOLID COMPOUNDS*

*Procedure :—*

Determine the m.p. of O.S., then refer, in the appropriate subsection, according to whether O.S. is yellow, orange, red, or green, to the list of m.p.s of compounds. If one of these m.p.s is identical with, or near to, that of O.S., apply any tests given for that compound, and prepare the derivative indicated. The method of preparation of phenylhydrazones is given on page 65.

**O.S. yellow.**

M.p.

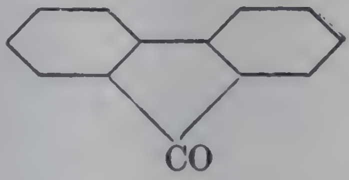
41° Benzalacetone. (Benzylideneacetone. Styryl methyl ketone.) $C_6H_5{\cdot}CH:CH{\cdot}CO{\cdot}CH_3$.

(*a*) To $\frac{1}{8}$-in. layer of a soln. of Br in $CCl_4$ in a dry t.t. add R.G. of O.S. and shake,
—deep brown colour disappears almost instantly, owing to the presence of a double bond in the molecule of O.S.

(*b*) Add R.G. of O.S. to 1 c.c. of cold conc. $H_2SO_4$ and shake,
—O.S. dissolves yielding an orange-red soln.

Phenylhydrazone, m.p. 156°.

84° Fluorenone. (Diphenylene ketone)
Phenylhydrazone, m.p. 151°.



95° Benzil. $C_6H_5{\cdot}CO{\cdot}CO{\cdot}C_6H_5$.

In a dry porcelain dish standing on a water bath place a pellet of KOH, then place on the top of it 2 R.G. of O.S. Carefully pour 1 c.c. of absolute alcohol down the side of the dish,—deep violet colour.

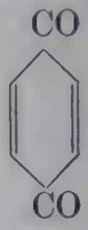
Evaporate to dryness, remove any undissolved KOH, add 1 c.c. conc. $H_2SO_4$, and gently rock the dish so that the acid runs over the whole of the residue,

M.p.

—intense red colour, due to the formation of benzilic acid, $(C_6H_5)_2C(OH)\cdot COOH$.

Diphenylhydrazone, m.p. 225°.

115° *p*-Benzoquinone.



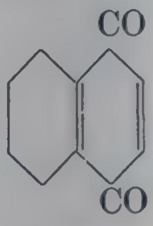
Peculiar pungent odour.

(*a*) To 2 c.c. KI soln. add one drop dil. $H_2SO_4$, then add R.G. of O.S., and shake,
—deep brown colour, due to liberated iodine.

(*b*) In a t.t. place the equivalent of $\frac{1}{8}$-in. layer of powdered $FeSO_4$ and an equal bulk of O.S. Add 2 c.c. dil. $H_2SO_4$ and shake. To the mixture add 5 c.c. water, and heat until a clear yellow soln. is obtained, then stand the t.t. in cold water,
—quinhydrone separates in fine, long green needles with a metallic lustre.

(*c*) *Preparation of phenoquinone (red), m.p.* 71°.
Dissolve in separate t.t.s in 3 c.c. hot ligroin $\frac{1}{8}$-in. layer of O.S. and $\frac{1}{8}$-in. layer of phenol. Mix the two solutions and cool. Filter off the red needles which separate from the yellow soln., recrystallise from ligroin, dry, and determine the m.p.

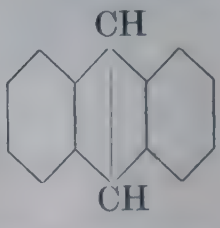
125° α-Naphthaquinone.



Pungent odour, similar to that of *p*-benzoquinone. Sparingly soluble in water, but dissolves in aq. NaOH yielding a red-brown soln.

130°–134° Benzoin. $C_6H_5\cdot CH(OH)\cdot CO\cdot C_6H_5$. Colourless when pure, but yellow samples will often be encountered.
See "Benzoin" (page 62).

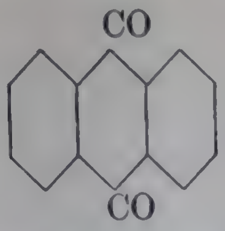
216° Anthracene.



Colourless when pure, but technical qualities are yellow.
See "Anthracene" (page 125).

M.p.

285° Anthraquinone.

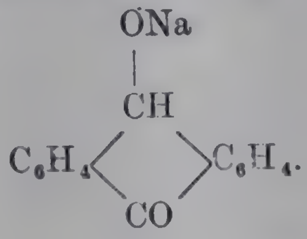


Insoluble in $NaHSO_3$ soln.

In a t.t. place 2 R.G. of O.S. and an equal bulk of zinc dust. Add 5 c.c. aq. NaOH, heat to boiling and continue boiling for ½ min.,
—deep red colour.

Filter while hot into a t.t. and shake,
—red colour rapidly disappears, owing to oxidation by the air, and a flocculent, pale yellow ppt. of anthraquinone separates. The phenomena described may be repeated by adding zinc dust, boiling, etc.

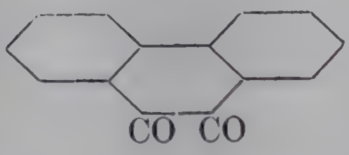
The red colour is due to the Na salt of oxanthranol,



**O.S. orange.**

M.p.

202° Phenanthraquinone.



(*a*) To ⅛-in. layer of O.S. in a t.t. add 3 c.c. of saturated $NaHSO_3$ soln. and warm the mixture,
—O.S. dissolves, and is repptd. on the addition of aq. NaOH.

(*b*) In a t.t. place 2 R.G. of O.S. and an equal bulk of zinc dust. Add 5 c.c. aq. NaOH, heat to boiling and continue boiling for ½ min. Filter the red brown soln. which is obtained,
—blue-green residue on the filter paper.

**O.S. red.**

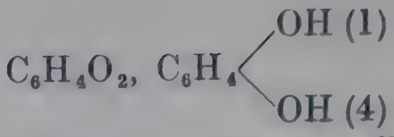
M.p.

71° Phenoquinone. $C_6H_4O_2,2C_6H_5OH$.

Place R.G. of O.S. in a porcelain dish, add a drop of dil. $NH_4OH$ and stir,
—blue-green colour.

**O.S. green.**

M.p.



171° Quinhydrone. $C_6H_4O_2, C_6H_4\left\langle\begin{matrix}OH\ (1)\\ OH\ (4)\end{matrix}\right.$ Readily soluble in cold alcohol, yielding a yellow soln.

Add R.G. of O.S. to Tollen's reagent (1 c.c. aq. $AgNO_3$, 1 c.c. aq. NaOH ; add dil. $NH_4OH$, drop by drop, until a clear colourless soln. is just obtained), —immediate grey-brown ppt.

If O.S. is

(*a*) a liquid, completely miscible with twice its volume of water, ascertain if it is identical with " Dioxane " (page 114); if it is not proceed as indicated under " Esters of carboxylic acids " (page 100).

(The following esters are completely miscible with twice their volume of water—methyl lactate, ethyl lactate, ethyl tartrate.)

(*b*) a solid, or a liquid, not completely miscible with twice its volume of water, proceed as follows :—

Weigh accurately a clean dry flask of 150 c.c. capacity, having a short wide neck and flat bottom. Add 1–1·5 g. of O.S. and weigh again. Add 25 c.c. of approximately N. alcoholic KOH and 3 c.c. water. Fit the flask with a cork and reflux condenser, place on a water bath, and allow the contents to boil gently for ½ hr. Meanwhile titrate 25 c.c. of the alcoholic KOH with N. HCl using phenolphthalein as the indicator. (N. $H_2SO_4$ gives a ppt. of $K_2SO_4$ with N. alcoholic KOH). When the contents of the flask have been heated for the required time, pour 10 c.c. water through the condenser into the flask. Also loosen the clamp holding the condenser and detach the latter from the flask, raising it so that the underside of the cork is about 1 in. above the mouth of the flask. Wash, by means of a wash bottle, that portion of the inner tube which projects through the cork, so that the wash water falls into the flask. Cool the contents of the flask, add phenolphthalein soln. and titrate the alkali present with N. HCl.

Work out the value of $x$ in the following expression

$$x = \frac{\text{Wt. of O.S.} \times 1{,}000}{\text{Difference between the two titrations} \times \text{factor of acid}}$$

If the value of $x$ is less than 500 proceed as indicated under " Esters of carboxylic acids " (page 100) otherwise see " Ethers and hydrocarbons " (page 114).

NOTE

The above procedure is essentially that described on page 112 for the determination of the equivalent weight of an ester. The highest equivalent weight of the esters named in this book is 238 (Benzyl cinnamate).

Theoretically no alkali would be used up by an ether or hydrocarbon.

If O.S. is shown to be an ester and subsequent work indicates that it is an alkyl ester, the equivalent weight may prove of value for identification purposes (see page 111). In such a case the blank test (described on page 112) should be carried out in order to obtain a more accurate result.

## ESTERS OF CARBOXYLIC ACIDS

Many esters possess agreeable odours, some of which resemble those of various fruits; some esters, however, are odourless.

### Identification by recognition of the products of hydrolysis—a carboxylic acid, and either an alcohol or a phenol.

If O.S. is a liquid follow the procedure given below; if a solid follow the procedure under " O.S. solid " (page 107).

***O.S. liquid.***

*Preliminary test.*

To 1 c.c. of the ester add 5 c.c. of 20% aq. KOH and shake. If a ppt. is formed (as will be the case with most esters of salicylic acid) the details of hydrolysis should be modified as indicated in the note at the end.

*Details of method of hydrolysis.*

Fit a 100-c.c. flask, having a short wide neck and flat bottom, with a cork and a reflux condenser. Remove the flask from the condenser, pour into it 25 c.c. of 20% aq. KOH and 5 c.c. of the ester, and add two or three pieces of porous pot. Connect the flask again to the condenser, heat the contents to boiling and continue boiling for the time indicated below.

NOTE.

In order to prevent " bumping," if a ppt. was obtained in the preliminary test, the KOH soln. should be heated alone in the flask almost to boiling and the ester added gradually through the condenser.

*Time of heating.*

If the ester is

(*a*) completely miscible with the aq. KOH, boil for 10 min.

(*b*) not completely miscible with the aq. KOH, boil fairly rapidly for 1 hr. unless the layer of ester disappears in a shorter period of time. In the latter case continue the boiling for a further period of about ⅓ of the time taken for the ester to disappear.

Notes.

(1) With esters of alcohols which are sparingly soluble in water there will always remain a layer of liquid on the surface of the aq. KOH.

The majority of such esters are completely hydrolysed in 1 hr.

(2) Hydrolysis is accelerated by periodically loosening the condenser clamp and giving the flask a rotary movement.

*Procedure after hydrolysis :—*

Allow the contents of the flask to cool somewhat, then pour 10 c.c. water through the condenser. Disconnect the flask and attach it to a sloping condenser. If no liquid is floating on the surface of the aq. KOH proceed as under **A** (below), otherwise as under **B** (page 102).

**A.** Distil, using a t.t. as the receiver, until 10 c.c. of distillate is obtained. (Ignore any slight milkiness which may be present in the distillate, due to a trace of unchanged insoluble ester passing over). Pour the alkaline residue in the flask into a beaker and keep it for the later treatment described on page 103. Rinse out the flask with water.

If the distillate possesses a pungent odour, resembling oil of mustard, apply the tests under "Allyl alcohol" (page 34), otherwise pour half the distillate into the empty flask which was used for the hydrolysis and add 20 c.c. dichromate mixture. (Keep the other half of the distillate in case of accident during the next procedure.)

If the dichromate is reduced (in which case the mixture will usually become green and hot within ½ min.) proceed as indicated below under "Identification of the alcohol."

If the dichromate is not reduced proceed as indicated under "No alcohol has been detected" (page 104).

*Identification of the alcohol.*

To the contents of the flask add 2–3 pieces of porous pot, connect the flask to the sloping condenser and use a t.t. (marked to indicate the space occupied by 7 c.c.) as the receiver. Distil until 7 c.c. is present in the receiver, noting if, when 2–3 c.c. is present, there is a layer of oil on the surface of the distillate. Proceed as under **A** (page 39). When the alcohol has been identified, proceed to identify the acid constituent of the ester in the manner described under "Treatment of the alkaline residue in the beaker" (page 103).

B.

NOTE.

In describing the procedure under (*a*) and (*b*), it is assumed, for the sake of clearness, that the ester has been completely hydrolysed and therefore the layer of liquid floating on the aq. KOH is an alcohol. The possibility of incomplete hydrolysis, and the procedure to be adopted in such a case, is dealt with under (*c*).

Distil, using a t.t. as the receiver, until about 3 c.c. of distillate is obtained.

If the distillate

(*a*) consists of two well-defined layers, continue distilling until the passage of oily drops through the condenser ceases. (The alcohol will form an upper layer, ½-in. or more deep.) Pour the alkaline residue in the flask into a beaker and keep it for future treatment.

Insert a 10-c.c. pipette into the distillate so that its point rests lightly on the bottom of the t.t. Draw up the whole contents of the t.t. into the pipette. Wait for a few seconds for all the small globules of alcohol to rise to the surface and unite, then allow the lower layer to run back into the t.t.

Run the alcohol into a dry t.t., add about ⅓ of its bulk of freshly ignited $K_2CO_3$, cork the tube and allow to stand for ½ hr. or more.

Meanwhile proceed to identify the acid constituent of the ester in the manner described under "Treatment of the alkaline residue in the beaker" (page 103).

When the alcohol is dry, determine its b.p. and refer to to the list of alcohols under "O.S. floats on water" (page 36).

(*b*) consists of a white emulsion, together with oily drops, which sink in the water, transfer the distillate, together with the cooled contents of the distillation flask, to a small separating funnel. Add 10 c.c. ether (see "Extraction with ether," page 21), shake and allow to stand until two well-defined layers are formed. Run off the lower layer into a beaker and keep this alkaline residue for future treatment. Pour the ethereal soln. through the neck of the funnel into a dry t.t. and add about ⅓ of the bulk of freshly ignited $K_2CO_3$. Cork the tube and allow to stand for ½ hr. or more. Meanwhile proceed to identify the acid constituent of the ester in the manner described under "Treatment of the alkaline residue in the beaker" (page 103).

When the ethereal soln. has stood for the necessary time, pour it into a dry flask, (that used for the hydrolysis, after rinsing out and drying, will be convenient) connect the flask to the water condenser and partly immerse it in hot water contained in a beaker. When all the ether has distilled off to the residue apply Test (*b*) under " Benzyl alcohol " (page 37).

(*c*) is clear and no upper layer is visible, collect about 15 c.c. of distillate. If there is found to be little or no upper layer in the t.t., or if the liquid (alluded to as " the alcohol ") obtained by the procedure under (*a*) or (*b*) cannot be identified as one of the alcohols under " O.S. floats on water " (page 36) or as benzyl alcohol, incomplete hydrolysis is indicated.

Repeat the hydrolysis as before but using 5 g. of solid KOH and 5 c.c. water instead of the 25 c.c. of 20% aq. KOH. Boil rapidly, with frequent shaking, for 2 hr. (Towards the end of the hydrolysis the contents of the flask may become semi-solid, owing to the separation of the K salt of the acid.) Allow to cool somewhat, add 30 c.c. water through the condenser, then proceed as under **B** (page 102).

*Treatment of the alkaline residue in the beaker.*

Cool the liquid if it is not already cold. (If it is found that the contents of the beaker have set to a solid mass, due to the separation on cooling of a sparingly soluble K salt, e.g. K cinnamate, redissolve the solid by carefully heating and add just sufficient water to prevent any solid separating again on cooling.)

Then carry out the procedure under the appropriate heading, either immediately below, or on page 104.

**An alcohol has been detected.**

Acidify 1 c.c. of the cooled alkaline soln. with a mixture of equal volumes of conc. $HNO_3$ and water (corresponding to roughly 30% $HNO_3$), cool and shake. (This concentration of acid is used in order that organic acids, such as phthalic acid, which are moderately soluble in water, may be pptd. No $KNO_3$ is deposited, even after cooling and shaking, when 20% aq. KOH is just acidified with 30% $HNO_3$.)

If (*a*) a ppt. separates, acidify the whole of the alkaline residue with 30% $HNO_3$, cool and shake. Filter off the pptd. organic acid, wash it with cold water and dry. Examine the acid in the manner described under **B** (page 74).

(*b*) no ppt. separates, proceed as under (1) if the acidified liquid possesses a rancid or unpleasant odour, otherwise as under (2).

(1) Acidify the whole of the alkaline liquid with 30% $HNO_3$ and add fused $CaCl_2$ until an oil separates. Extract the oil in the manner described for the alcohol under (*b*) page 102, but using fused $CaCl_2$ as the drying agent.

Determine the b.p. of the oil and refer to the list of b.p.s of liquid acids (page 68).

(2) Acidify 2 c.c. of the alkaline soln. with glacial acetic acid, heat to boiling and add 2 or 3 drops of aq. $CaCl_2$; a white ppt. indicates an oxalate.

If no white ppt. is obtained just acidify the whole of the alkaline soln. with 50% $H_2SO_4$, add conc. $NH_4OH$ until just alkaline, cool and filter off any $K_2SO_4$ which may have separated. Boil until the soln. is neutral, cool a portion and proceed as indicated under A, Test (*b*) page 87.

If a solid salt is required for confirmatory tests evaporate some of the neutral soln. to dryness in a basin, heating over a gauze until spirting commences, then completing the removal of water by heating on a sandbath with rapid stirring. In tests, however, which involve warming with conc. $H_2SO_4$, e.g. the guaiacol test for a lactate and the fluorescein test for a succinate, the original ester will give the same result as the solid salt.

If only negative results are obtained, add 10 c.c. of conc. $NH_4OH$ to 2 c.c. of the original ester and allow to stand for ½ hr. with periodic shaking. If a crystalline ppt. is formed, filter it off, wash it with cold water, dry, and determine the m.p., then refer to the list of m.p.s of acid amides (page 180) in order to identify the acid constituent of the ester.

**No alcohol has been detected.**

The alkaline residue will contain a phenoxide, or a polyhydric alcohol.

*Procedure :—*

Pour the alkaline residue into a 100-c.c. cylinder and make up to 50 c.c. with water. Pass a fairly rapid current of $CO_2$ (which has been washed with water) through the liquid until 1 c.c., after the addition of 10 c.c. aq. $BaCl_2$, gives no colour on adding phenolphthalein soln. (This indicates that no free KOH is present and therefore any original phenoxide, which would be partially hydrolysed by water to the free phenol and KOH, is completely decomposed.)

Usually the passage of $CO_2$ for 15 min. is sufficient.

If (*a*) a considerable amount of solid separates, filter it off (keep the alkaline filtrate), wash it with cold water to remove the K salt of the acid and $K_2CO_3$ and dry. Apply Test 1 (page 29) and see "Phenolic compounds" (page 44).

Extract the alkaline filtrate with ether, exactly as described under (*b*) in order to remove any phenol left in soln., which would interfere with the tests for acids, especially the $FeCl_3$ test. Identify the acid constituent of the ester in the alkaline filtrate in the manner described under "An alcohol has been detected" (page 103).

(*b*) little or no solid separates, or an emulsion is formed, transfer the liquid to a separating funnel, add 10 c.c. ether and shake. (See "Extraction with ether," page 21). Allow to stand until two well-defined layers are formed, then run off the lower aq. layer into a beaker. Pour the ethereal extract into another vessel, return the alkaline liquid to the separating funnel, add 10 c.c. ether and proceed as before. Repeat the process a third time, leaving the ether soln. this time in the funnel and retain the alkaline liquid in the beaker. Pour the other two ether extracts into the funnel and allow to stand for a time, then run off any lower aqueous layer which separates. Dry the ether soln. by allowing it to stand in contact with freshly ignited $K_2CO_3$ for as long a period as convenient, then pour the liquid through the neck of the funnel into a dry flask (that used for the hydrolysis is convenient) and attach the flask to the water condenser. Distil off the ether by partially immersing the flask in hot water contained in a beaker.

If a residue is obtained apply Test 1 (page 29), then see "Phenolic compounds" (page 44).

*Treatment of the alkaline residue in the beaker.*

If (*a*) a phenol has been detected, proceed as indicated under "An alcohol has been detected" (page 103), in order to identify the acid constituent of the ester.

(*b*) no phenol has been detected, just acidify the whole of the alkaline residue with 50% $H_2SO_4$, add conc. $NH_4OH$ until just alkaline, cool and filter off any $K_2SO_4$ which may have separated. Evaporate to dryness in a basin and cool. Stir the solid or semi-solid residue with 10–15 c.c. of a mixture of two volumes of absolute alcohol and one volume of ether; filter. Wash the residue on the filter with 5 c.c. of the alcohol-ether mixture, allowing the filtrate to run into the previous one. To the residue on the filter apply Test (*b*) under A (page 87), in order to identify the acid constituent of the ester. Transfer the filtrate to a dry flask (that used for the hydrolysis is convenient), attach the flask to the water condenser and partially immerse the former in boiling water contained in a beaker. When the alcohol and ether have distilled off, examine the syrupy residue (which will usually contain solid matter) for the presence of ethylene glycol or glycerol (see pages 41, 42).

In the following lists, the time required for the complete hydrolysis of some of the commoner liquid esters (using 20% aq. KOH, or equal weights of KOH and water) is given.

**Hydrolysis with 20% aq. KOH.**

*Esters, of which the alcoholic constituent is miscible with water*

| *B.p.* | | *Minutes* |
|---|---|---|
| 32° | Methyl formate | 5 |
| 54° | Ethyl formate | 15 |
| 57° | Methyl acetate | 15 |
| 77° | Ethyl acetate | 15 |
| 79° | Methyl propionate | 10 |
| 91° | *iso*-Propyl acetate | 30 |
| 98° | Ethyl propionate | 20 |
| 101° | *n*-Propyl acetate | 20 |
| 102° | Methyl *n*-butyrate | 15 |
| 120° | Ethyl *n*-butyrate | 30 |
| 145° | Methyl lactate | 10 |
| 154° | Ethyl lactate | 10 |
| 181° | Methyl malonate | 10 |
| 186° | Ethyl oxalate | 5 |
| 187° | Ethylene glycol diacetate | 10 |
| 195° | Methyl succinate | 10 |
| 198° | Ethyl malonate | 15 |
| 198° | Methyl benzoate | 30 |
| 213° | Ethyl benzoate | 45 |
| 216° | Ethyl succinate | 20 |
| 218° | Methyl phenylacetate | 15 |
| 224° | Methyl salicylate | 15 |
| 229° | Ethyl phenylacetate | 30 |
| 234° | Ethyl salicylate | 5 |
| 258° | Glycerol triacetate (Triacetin) | 10 |
| 271° | Ethyl cinnamate | 60 |
| 280° | Ethyl tartrate | 5 |
| 282° | Methyl phthalate | 30 |
| 294° | Ethyl citrate | 5 |
| 298° | Ethyl phthalate | 60 |

*Esters of which the alcoholic constituent is not miscible with water*

| *B.p.* | | |
|---|---|---|
| 98° | *iso*-Butyl formate | 1 hr. |
| 107° | *n*-Butyl formate | ,, |
| 116° | *iso*-Butyl acetate | ,, |
| 124° | *iso*-Amyl formate | ,, |
| 126° | *n*-Butyl acetate | ,, |
| 139° | *iso*-Amyl acetate | ,, |
| 188° | *n*-Butyl lactate | ,, |
| 203° | Benzyl formate | ,, |
| 216° | Benzyl acetate | ,, |
| 228° | Benzyl propionate | ,, |
| 268° | *n*-Butyl salicylate | ,, |
| 277° | *iso*-Amyl salicylate | ,, |
| 320° | Benzyl salicylate | ,, |

*Phenolic esters*

| *B.p.* | | *Minutes* |
|---|---|---|
| 196° | Phenyl acetate | 5 |
| 278° | Resorcinol diacetate | 10 |

### Hydrolysis with equal weights of KOH and water

| *B.p.* | | |
|---|---|---|
| 241° | *iso*-Butyl benzoate | 1–2 hr. |
| 249° | *n*-Butyl benzoate | ,, |
| 262° | *iso*-Amyl benzoate | ,, |
| 318° | Benzyl phenylacetate | ,, |
| 323° | Benzyl benzoate | ,, |
| 338° | *n*-Butyl phthalate | ,, |
| 349° | *iso*-Amyl phthalate | ,, |

### *O.S. solid.*

*Procedure :—*

Determine the m.p. of O.S. and apply the following test :—

To $\frac{1}{8}$-in. layer of O.S. in a t.t. add an amount of solid KOH roughly equal in bulk to a pea and 2 c.c. alcohol. Heat to boiling and continue boiling for $\frac{1}{2}$ min.

If a dark brown or green colour develops proceed as indicated under **C** (page 109); otherwise as under **A** if m.p. 80° or below, or under **B** (page 109) if m.p. above 80°.

**A.** Fit a 100-c.c. flask, having a short wide neck and flat bottom, with a cork and a reflux condenser. Remove the flask from the condenser and place in it 5 g. solid KOH, 5 c.c. water, 2 g. of O.S. and some porous pot. Connect the flask again to the condenser, heat the contents to boiling and continue boiling for $\frac{1}{2}$ hr. unless the ester completely disappears in a shorter period of time. (Some methyl esters and also some phenolic esters will be completely hydrolysed in 5 min. or less.)

If (*a*) no oil is present on the surface of the aq. KOH, allow the contents of the flask to cool somewhat, add 30 c.c. water through the condenser, then proceed exactly as described under **A** (page 101).

Also refer to list **A** (page 110), in order to ascertain (by taking into account the m.p. of O.S.) the alcohol or phenol and acid likely to be present and proceed accordingly. If, on account of the m.p., and the proved absence of a phenoxide in the alkaline residue, it is suspected that O.S. is either ethylene glycol dibenzoate or glyceryl tribenzoate, the procedure described under (*b*) page 105, should be modified as follows :—

Acidify the alkaline residue with a mixture of equal volumes of conc. $HNO_3$ and water ; cool. Filter off the pptd. acid and apply tests for benzoic acid. To the filtrate add conc. $NH_4OH$ until just alkaline. Evaporate, etc., as described under (*b*) page 105.

(*b*) an oil is present on the surface of the aq. KOH, allow the contents of the flask to cool somewhat, then add 10 c.c. alcohol through the condenser. Heat to boiling and continue boiling gently for 15 min.

Remove the flask from the condenser and boil the contents until an oily upper layer separates. (See note below.) Add 10 c.c. water, cool and pour into a separating funnel. Add 10 c.c. ether (see " Extraction with ether," page 21), shake, allow to stand until two well-defined layers are formed, then run off the lower layer into a beaker and keep this alkaline residue for future treatment. Pour the ether soln. into a dry flask (that used for the hydrolysis will be convenient), connect to a water condenser and partially immerse the flask in hot water contained in a beaker. When the ether has distilled off, add 5 drops of the residue to 2 c.c. dichromate mixture and warm slightly.

A strong, bitter-almond odour of benzaldehyde indicates that the residue is benzyl alcohol.

NOTE.

If during the boiling down, solid separates and causes " bumping " (as will happen if the ester is benzyl cinnamate) add 10 c.c. water, continue boiling until solid again separates, add 20 c.c. water, heat until all the solid has dissolved, then cool. Extract with 10 c.c. ether, etc.

*Identification of the acid constituent of the ester.*

Refer to List B of m.p.s of benzyl esters (page 110), and proceed as follows :—

If the m.p. of O.S. is 80° or near, acidify 2 c.c. of the alkaline residue with glacial acetic acid, heat to boiling and add 2 or 3 drops aq. $CaCl_2$. A white ppt. indicates an oxalate.

If the m.p. of O.S. is 42° or below, apply Test (*b*) under " Phthalic anhydride " (page 76), using R.G. of O.S.

A yellow-green fluorescence indicates that O.S. is a phthalate or succinate.

To distinguish apply Test (*a*) under " Phthalic anhydride " (page 76), using R.G. of O.S. If the red colour of phenolphthalein is obtained O.S. is a phthalate, otherwise a succinate.

If no yellow-green fluorescence is obtained, acidify the alkaline residue with a mixture of equal volumes of conc. $HNO_3$ and water. Filter off the pptd. organic acid, wash it with water and dry. Apply the test under " Cinnamic acid " (page 78).

**B.** In the flask of a reflux apparatus place 5 g. of solid KOH 25 c.c. of alcohol and 2 g. of ester. Heat the contents of the flask to boiling and continue boiling gently for 15 min. Add 25 c.c. water and distil off 20–25 c.c. of liquid in order to remove most of the alcohol. Pour the residue in the flask into a 100-c.c. cylinder, make up to 50 c.c. with water and proceed as indicated under " No alcohol has been detected," page 104). Also refer to list *C* (page 111), in order to ascertain (by taking into account the m.p. of O.S.) the phenol and acid likely to be present and proceed accordingly.

NOTE.

The above procedure is intended for the hydrolysis of the common phenolic esters which are very stable towards aqueous KOH. It is possible, however, that O.S. may be one of the less common alkyl esters, e.g. ethyl *p*-hydroxybenzoate, m.p. 116°, methyl *p*-hydroxybenzoate, m.p. 131°, methyl terephthalate, m.p. 140°.

If, therefore, no phenol is detected, the hydrolysis should be repeated, using aq. KOH in the manner described under A (page 107).

**C.** Proceed as under **B** (above) and add the equivalent of ½-in. layer of zinc dust in a t.t. in order to minimise oxidation. Filter off the zinc after the passage of $CO_2$.

The only esters of polyhydric phenols likely to be encountered are acetates and benzoates. Owing to the dark-coloured solutions usually obtained the test for an acetate with $FeCl_3$

will be unsatisfactory, while the pptd. benzoic acid will be discoloured and difficult to obtain white by crystallisation. Satisfactory results may be obtained as follows:—

If a ppt. has been obtained on acidifying the alkaline residue with $HNO_3$, filter it off, transfer it to the hydrolysis flask and add 30 c.c. of 25% $H_2SO_4$. Connect the flask to the water condenser and distil until about 10 c.c. of distillate is obtained. Pure white benzoic acid will collect in the condenser tube and may be washed out and filtered off.

If no ppt. has been obtained on acidifying 1 c.c. of the alkaline residue with $HNO_3$, acidify the remainder of the alkaline residue with 50% $H_2SO_4$. Pour 25 c.c. of the acidified soln. into the hydrolysis flask, add 25 c.c. of 50% $H_2SO_4$, connect the flask to the water condenser and distil over 10 c.c. of liquid. To the distillate add $NH_4OH$ until just alkaline and boil until neutral.

To 2 c.c. of the neutral soln. add an equal volume of aq. $FeCl_3$,—wine red colour (viewed through the depth of the liquid) indicating an acetate.

See list *D* for m.p.s of common esters.

*List A.* Methyl esters; esters of phenols and of polyhydric alcohols.

NOTE.

Except in the case of glyceryl tribenzoate, the time given refers to the hydrolysis of 2 g. with 25 c.c. of 20% aq. KOH. A considerably shorter time is required when 5 g. solid KOH + 5 c.c. water are used.

| *M.p.* | | *Time (in min.) required for hydrolysis* |
|---|---|---|
| 36° | Methyl cinnamate | 15 |
| 42° | Phenyl salicylate (Salol) | 10 |
| 48° | Methyl tartrate | 5 |
| 54° | Methyl oxalate | 5 |
| 57° | Guaiacol benzoate | 30 |
| 68° | Phenyl benzoate | 20 |
| 70° | β-Naphthyl acetate | 5 |
| 71° | *p*-Cresyl benzoate | 45 |
| 73° | Ethylene glycol dibenzoate | 60 |
| 76° | Glyceryl tribenzoate | 30 (with 5 g. KOH + 5 c.c. water) |
| 78° | Phenyl carbonate | 10 |

*List B.* Benzyl esters. Hydrolysed in 15 min. with alcoholic KOH. See under (*b*), page 108.

| *M.p.* | |
|---|---|
| 39° | Benzyl cinnamate |
| 42° | Benzyl phthalate |
| 42° | Benzyl succinate |
| 80° | Benzyl oxalate |

*List C.* Phenolic esters. Hydrolysed in 15 min. with alcoholic KOH. (See under **B**, page 109.)

| *M.p.* | |
|---|---|
| 86° | Guaiacol carbonate |
| 95° | β-Naphthyl salicylate (Betol) |
| 107° | β-Naphthyl benzoate |

*List D.* Esters of polyhydric phenols. Hydrolysed in 15 min. with alcoholic KOH. (See under **C**, page 109.)

| *M.p.* | |
|---|---|
| 63° | Catechol diacetate |
| 84° | Catechol dibenzoate |
| 117° | Resorcinol dibenzoate |
| 123° | Quinol diacetate |
| 161° | Pyrogallol triacetate |
| 199° | Quinol dibenzoate |

## Quantitative hydrolysis of pure esters.

The determination of the equivalent weight of an ester is valuable for the following purposes :—

(*a*) To ascertain the actual number of acid radicals in the molecule of esters of polyhydric alcohols.

EXAMPLE.

The equiv. wt. of a certain glyceryl benzoate, determined in the manner described on page 112, was found to be 135·7.

The following are the equivalent weights of the three possible glyceryl benzoates, calculated from the molecular formulæ :—

| | |
|---|---|
| Monobenzoate . . . | 196·1 |
| Dibenzoate . . | 150·1 |
| Tribenzoate . . . | 134·7 |

Obviously the ester in question is the tribenzoate.

(*b*) To determine the equivalent weight of the acid in an ester of a monohydric alcohol when the alcohol, but not the acid, has been identified.

The equiv. wt. of the ester is first found by the method described on page 112.

The equiv. wt. of the acid is obtained from this by subtracting the formula weight of the alkyl radical and adding 1 for the H which the alkyl radical has replaced in the acid.

EXAMPLE.

The equiv. wt. of an ethyl ester was found to be 80·4.

Equiv. wt. of acid = 80·4 − 29·0 (formula wt. of $C_2H_5$—) + 1 = 52·4.

On referring to the list of equivalent weights of common acids (page 86) it will be found that the figure obtained is very close to the equivalent weight of malonic acid. Hence the ester is possibly ethyl malonate.

This is particularly useful as an aid to the identification of acids which are readily soluble in water and for whose salts there are no characteristic reactions.

*Practical details.*

Weigh accurately a clean, dry flask of 150 c.c. capacity, having a short wide neck and flat bottom. Add 1–1·5 g. of the ester and weigh again.

Into this flask and also into another similar one, introduce 25 c.c. of approximately N. alcoholic KOH and 3 c.c. of water. (The water is necessary to prevent the separation of K salts, such as K phthalate, which would cause violent bumping.)

Fit each flask with a cork and reflux condenser and place on a water bath. Allow the contents of the flasks to boil very gently for ½ hr. (This time has been found to be sufficient for very stable esters, such as amyl benzoate, benzyl benzoate, *n*-butyl phthalate, glyceryl tribenzoate.)

Pour 10 c.c. of water through each condenser, also loosen the clamp holding the condenser and detach the latter from the flask, raising it so that the under side of the cork is about 1 in. above the mouth of the flask. Wash, by means of a wash bottle, that portion of the inner tube which projects through the cork, so that the wash water falls into the flask. Cool the contents of each flask, add phenolphthalein and titrate the alkali present with N. HCl (N. $H_2SO_4$ gives a ppt. of $K_2SO_4$ with N. alcoholic KOH)

NOTE.

The blank experiment is necessary in order to determine the acid equivalent of the volume of alcoholic KOH employed, since the latter is liable to alter in strength on heating in a glass vessel, owing to a tendency for the alcohol to become oxidised by the air, with subsequent resinification of the aldehyde formed, and also owing to a solvent action on the glass.

If the ester is one which is readily hydrolysed (for example, in 15 min. by 20% aq. KOH) and yields a water-soluble alcohol, aqueous N. NaOH may be employed.

In this case boil the contents of the flask gently over a gauze, noting the time taken for the layer of ester to disappear entirely, then continue boiling for a further period of about $\frac{1}{3}$ of this time. If the ester is miscible with the NaOH soln., boil for 15 min.

If $v$ c.c. = the difference between the two titrations
and $w$ g. = the weight of ester taken

$$\text{Equiv. wt. of ester} = \frac{w \times 1{,}000}{v \times \text{factor of acid}}$$

### β-Ketonic esters

B.p.
181° **Ethyl acetoacetate.** $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COO\ Et.$

Fit a 100-c.c. flask, having a short wide neck and flat bottom, with a cork and a reflux condenser. Remove the flask from the condenser, pour into it 25 c.c. of 20% aq. KOH and 5 c.c. of O.S. and add some porous pot. Connect the flask again to the condenser, heat the contents to boiling and continue boiling for 5 min. Allow the contents of the flask to cool somewhat, then pour 10 c.c. water through the condenser. Disconnect the flask and attach it to a sloping condenser. Distil, using a t.t. as the receiver, until 10 c.c. of distillate is obtained. Pour the alkaline residue in the flask into a beaker and keep it for the treatment described below. Rinse out the flask with water.

*Treatment of the distillate.*

(*a*) To 2 c.c. add an equal volume of $\frac{1}{2}$% aq. sodium nitroprusside, then add 2 drops aq. NaOH. A wine-red colour, which is changed to violet-red on acidifying with acetic acid, indicates that acetone is one of the products of hydrolysis.

(*b*) Pour the remainder of the distillate into the empty flask which was used for the hydrolysis and add 20 c.c. dichromate mixture and some porous pot. Connect the flask to the sloping condenser and distil, using a t.t. as the receiver, until 5 c.c. of distillate is obtained. To 2 c.c. of the distillate add an equal volume of 20% aq. KOH, heat to boiling and continue boiling for $\frac{1}{2}$ min. A yellow soln., followed by a yellow ppt., changing to orange, with a disagreeable odour (due to the formation of acetaldehyde resin) indicates that ethyl alcohol is one of the products of hydrolysis.

*Treatment of the alkaline residue in the beaker.*

Acidify with 50% $H_2SO_4$; a vigorous effervescence indicates the presence of $K_2CO_3$.

FeCl$_3$; a wine-red colo
depth of the liquid) indic
acetate.

Thus with 20% aq. KOH
hydrolysis occur, the fo
K$_2$CO$_3$ and ethyl alcohol,
and ethyl alcohol.

## ETHERS AND HYDR

If O.S. is a liquid proceed as indicated
the procedure under " O.S. solid " (page

***O.S. liquid.***

Determine the b.p., then refer, in th
according to whether O.S. is completel
volume of water, floats on water, or si
to the list of b.p.s of ethers and hydro
b.p.s is identical with, or near to, that of
of O.S. by applying to it any tests gi
determining the m.p. of the derivati
sections on " Crystallisation " and "
pages 16–21).

NOTE :

Each of the liquids in this section
odour which, however, can only be desc

**O.S. completely miscible with twice**

B.p.
101° Dioxane. (Diethylene dioxide.

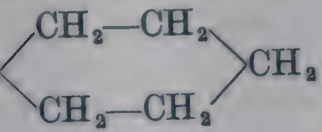
In a boiling tube place th
in a t.t. of solid KMn
and 5 drops of O.S.

Heat the liquid to boiling,
then filter. Destroy
the addition of H$_2$O$_2$.

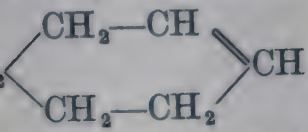
Acidify 2 c.c. of the filtra

quantity of the hydrocarbon or ether is
mine in carbon tetrachloride. Saturated
decolourisation. with evolution of fumes
bstitution.
substitution may occur simultaneously,
ic ethers.
be identical with one of the compounds
ee “ Additional compounds ” (page 128).

lexahydrobenzene.)



'etrahydrobenzene.)



drops of O.S. to $\frac{1}{8}$-in. layer in a t.t. of a
Br in $CCl_4$; shake. If the colour of the

emoved in a second or so, *cyclo*hexene is
cated. Oxidise O.S. to adipic acid, m.p.
°, as follows :—
nto a 100-c.c. wide-mouthed flask pour
c. of O.S. and 30 c.c. dichromate mixture
add two or three pieces of porous pot.
the flask with a reflux condenser, heat the
tents to boiling and continue boiling for
ır.
Cool and shake, then filter. Wash the solid
efully with cold water, crystallise from
ter, dry, and determine the m.p.
unaltered, add one drop of O.S. to 1 c.c. of
mixture of equal volumes of conc. $HNO_3$
d conc. $H_2SO_4$, shake for ½ min., then pour
o 10 c.c. water contained in a dish.
A bitter-almond odour (due to the forma-

B.p.

*preparation from it of* m-*dinitrobenzene*, m.p. 90°, as follows :—

Pour 1 c.c. of O.S. into a dry 100-c.c. flask and add a mixture of 3 c.c. each of conc. $HNO_3$ and conc. $H_2SO_4$. Heat to boiling and continue boiling for ½ min. Cool, pour into 50 c.c. water, cool and shake. Filter, wash the solid with cold water, crystallise twice from alcohol, dry, and determine the m.p.

(2) *cyclo*Hexane is unaffected by the treatment.

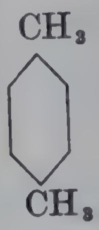
110° Toluene. $C_6H_5{\cdot}CH_3$.

*Preparation of 2 : 4-dinitrotoluene, m.p. 70° :—*

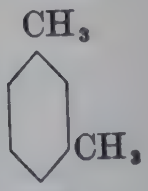
Pour 1 c.c. of O.S. into a dry 100 c.c. flask and add quickly a mixture of 3 c.c. each of fuming $HNO_3$ and conc. $H_2SO_4$. (The reaction is violent.) Cool, pour into 50 c.c. water ; cool and shake. Filter, wash the solid with cold water, crystallise twice from alcohol, dry, and determine the m.p.

136° Ethylbenzene. $C_6H_5{\cdot}CH_2{\cdot}CH_3$.

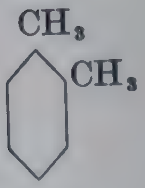
138° *p*-Xylene.



139° *m*-Xylene.



142° *o*-Xylene.



*Oxidation test :—*

Into a 150 c.c. wide-mouthed flask pour 1 c.c. of O.S. and add 5 g. solid $KMnO_4$, 80 c.c. water, 10 drops aq. NaOH and two or three pieces of porous pot. Fit the flask with a reflux condenser, heat the contents to boiling and continue boiling fairly rapidly for 2 hr. Cool, and pass $SO_2$ until any purple colour and the brown ppt. have disappeared.

If (*a*) a clear soln. is obtained, filter from unchanged hydrocarbon, *cool well and shake vigorously.* Filter off the solid which crystallises out, wash it carefully with cold water and dry. Apply tests for phthalic acid (page 77).

Positive results indicate that O.S. is *o*-xylene. Confirm the identity of O.S. by preparing *o*-xylenesulphonamide (see below).

If negative results are obtained, determine the m.p. of the solid. A m.p. of 121° (or near) indicates that the oxidation product is benzoic acid and that O.S. is ethylbenzene.

(*b*) a bulky white ppt. is obtained, filter, wash the solid with water and dry. Apply the test given under isophthalic and terephthalic acids (page 78), and distinguish between the acids by preparing the dimethyl ester.

Identification of the solid as (1) isophthalic acid, indicates that O.S. is *m*-xylene.

(2) terephthalic acid, indicates that O.S. is *p*-xylene.

*Preparation of* o-*xylenesulphonamide, m.p. 144°.*

To 1 c.c. of the hydrocarbon in a dry t.t. add 2 c.c. conc. $H_2SO_4$, immerse the end of the t.t. in boiling water and shake until the hydrocarbon has completely dissolved. (½–1 min.) Cool and pour into 20 c.c. of a saturated soln. of common salt. Cool, and shake or stir vigorously. Filter off the ppt. of sodium xylenesulphonate and wash it with saturated salt soln. Dry the ppt. thoroughly in a steam oven. Place the dried salt in a porcelain dish, add 4 g. $PCl_5$ and grind the two substances intimately together with a pestle. Heat on a rapidly boiling water bath for 10 min. stirring the mixture periodically. Cool the mixture, add 10 c.c. cold water and stir. Wash the contents of the dish into a separating funnel and extract with ether (see page 21). Distil off the ether, thoroughly mix the residue of sulphonyl chloride with

B.p.

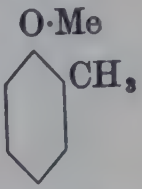
2 g. powdered ammonium carbonate, and heat on a rapidly boiling water bath for 15 min. Cool, add 20 c.c. cold water, stir well and filter. Wash the sulphonamide with water, crystallise it from alcohol, dry, and determine the m.p.

154° Anisole. (Phenyl methyl ether.) $C_6H_5 \cdot O \cdot CH_3$.

*Preparation of dinitroanisole*, m.p. 88° :—

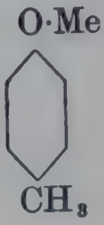
Dissolve 1 c.c. of O.S. in 5 c.c. conc. $H_2SO_4$; cool. Add 1 c.c. conc. $HNO_3$ in portions (about 5 drops at a time) cooling after each addition. Pour into 20 c.c. water, cool and shake. Filter, wash the solid with cold water, crystallise from a small quantity of alcohol, dry, and determine the m.p.

171° *o*-Cresyl methyl ether.

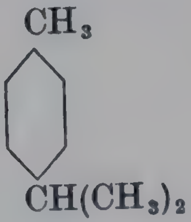


172° Phenetole. (Phenyl ethyl ether.) $C_6H_5 \cdot O \cdot Et$.

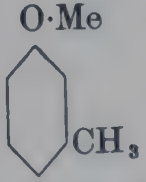
175° *p*-Cresyl methyl ether.



175° *p*-Cymene.



177° *m*-Cresyl methyl ether.



To 1 c.c. of O.S. add 1 c.c. of conc. $H_2SO_4$; gently shake.

If O.S.

A. does not dissolve completely in the conc. $H_2SO_4$, pour 1 c.c. of O.S. into a 100-c.c. wide-mouthed flask, add 30 c.c. dichromate mixture and two or three pieces of porous pot. Fit the flask with a reflux condenser, heat the contents of the flask to boiling and continue boiling fairly rapidly for 3 hr. Add 50 c.c. water and filter.

Wash the solid with water until free from Cr compounds and dry. Apply the test for terephthalic acid (page 78). A positive result indicates that O.S. is *p*-cymene.

B. Dissolves completely in the conc. $H_2SO_4$ (soln. may be yellow, pink, or light red brown in colour), add another 9 c.c. of conc. $H_2SO_4$ and cool. Add 1 c.c. conc. $HNO_3$ in portions (about 5 drops at a time), cooling after each addition. (Soln. will become reddish or greenish brown.) Pour into 50 c.c. water, cool and shake.

If (*a*) a pale yellow emulsion is obtained, yielding a pale yellow solid on shaking, filter. Wash the solid well with cold water, crystallise from alcohol, dry, and determine the m.p.

M.p. of nitro derivative :—

67° indicates that O.S. is *o*-cresyl methyl ether

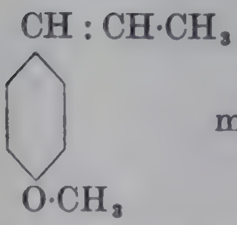
86° indicates that O.S. is phenetole

91° indicates that O.S. is *m*-cresyl methyl ether.

(*b*) no yellow emulsion is formed, but the mixture froths on pouring into water, yielding an orange-brown soln. with little or no solid, proceed with the oxidation test described under “ B.p. 136°–142° ” (page 116), using 2½ g. solid $KMnO_4$, 40 c.c. water, 5 drops aq. NaOH and 1 c.c. of O.S. The $KMnO_4$ will usually be completely reduced in 1¼ hr.

Identification of the oxidation product as anisic acid, m.p. 184°, indicates that O.S. is *p*-cresyl methyl ether.

232° Anethole.



$CH:CH{\cdot}CH_3$ / $C_6H_4$ / $O{\cdot}CH_3$

m.p. 21°. Odour of aniseed.

(*a*) To ⅛-in. layer in a t.t. of a soln. of Br in $CCl_4$ add 3 drops of O.S. ; shake.
—brown colour rapidly disappears, due to the presence of a double bond in the molecule of O.S.

(*b*) *Oxidation to anisic acid*, m.p. 184°.

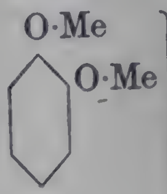
Into a 250-c.c. flask pour 50 c.c. dichromate mixture and 1 c.c. of O.S. Heat, shaking round frequently, until a vigorous reaction commences, then remove the flame. When the vigorous reaction has ceased, cool, filter off the solid, and wash it with water to remove green Cr salt. Add the solid to 20 c.c. boiling dil. HCl, then add a few crystals of $Na_2SO_3$, boil and stir for 5 min. Add 10 c.c. conc. $NH_4OH$, boil for 5 min., then cool and filter. Acidify the filtrate with conc. HCl, filter off the solid, wash it with water, crystallise from dilute alcohol, dry, and determine the m.p.

**O.S. sinks in water.**

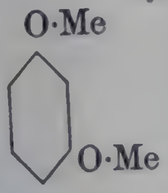
See notes under "O.S. floats on water" (page 115).

B.p.

205° Catechol dimethyl ether (Veratrole)



214° Resorcinol dimethyl ether



Distinguish by dibromo derivative.

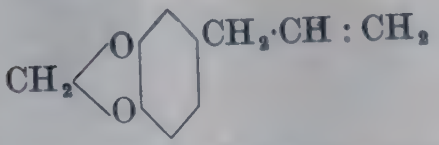
*Preparation of dibromo derivative.* (The bromination should be carried out in a fume cupboard.)

Into a 100-c.c. flask pour 1 c.c. of O.S. and add 1 c.c. bromine. When the vigorous reaction has ceased, add 20 c.c. aq. NaOH and shake. Dilute with water, filter, wash the solid with cold water, crystallise from alcohol, dry, and determine the m.p.

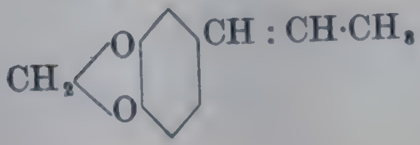
(If the product possesses a brown colour, recrystallise until it becomes white.)

M.p. 91° indicates dibromo catechol dimethyl ether.
" 141° " " resorcinol " "

232° Safrole.



246° *iso*-Safrole.

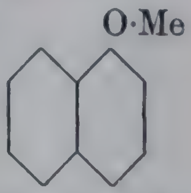


B.p. To $\frac{1}{8}$-in. layer in a t.t. of a soln. of Br in $CCl_4$ add 3 drops of O.S. and shake.

—brown colour rapidly disappears, due to the presence of a double bond in the molecule of O.S.

Alkaline $KMnO_4$ → piperonylic acid, m.p. 228°.

263° α-Naphthyl methyl ether.



To 2 c.c. of a cold saturated soln. of picric acid in benzene add 2 drops of O.S.,

—red crystals of a picrate form.

% methoxyl radical = 19·6.

***O.S. solid.***

*Procedure for the identification of O.S.* (See Note 2, page 115.)

Determine the m.p., then refer to the list of m.p.s of hydrocarbons and ethers. If one of these m.p.s is identical with, or near to, that of O.S., apply any tests given, and prepare the derivative there indicated. (See sections on "Crystallisation" and "Drying of substances," pages 16–21.)

In the case of ethers, where no derivative is indicated, determine the b.p. and also the percentage of methoxyl or ethoxyl radical. (For method of determination, see page 126.)

M.p.

21° Anethole. Crystalline mass. Odour of aniseed. B.p. 232°. See "Anethole" under "O.S. floats on water" (page 119).

26° Diphenylmethane. $C_6H_5{\cdot}CH_2{\cdot}C_6H_5$. Crystalline mass. Odour resembling oranges. B.p. 261°.

*Oxidation to benzophenone*, $C_6H_5{\cdot}CO{\cdot}C_6H_5$, identified by conversion to its phenylhydrazone, m.p. 137°.

Weigh out in a 100-c.c. flask 1 g. of $CrO_3$. Add a mixture of 1 c.c. water and 9 c.c. glacial acetic acid, heat to boiling and continue boiling gently. Dissolve 1 c.c. of molten O.S. in 9 c.c. glacial acetic acid, then add the soln. gradually to the contents of the flask. Boil gently for 5 min., cool, and pass $SO_2$ to reduce the excess of chromic acid. Add 50 c.c. water, extract with 20 c.c. ether (see page 21), and wash the ethereal soln. three times with 3 c.c. water. Distil off the ether, add a boiling soln. of 5 drops phenylhydrazine in 1 c.c. glacial acetic acid, heat 5 min. on a water bath, cool and stir until solid separates. Stir with 3 c.c.

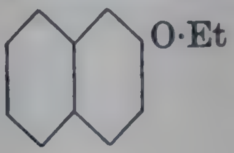
M.p. alcohol, filter and wash the solid with alcohol. Crystallise the solid twice from alcohol, dry, and determine the m.p.

28° Diphenyl ether. (Diphenyl oxide.) $C_6H_5{\cdot}O{\cdot}C_6H_5$. Crystalline mass. Geranium-like odour. B.p. 252°.

*Preparation of 4·4′-dinitro derivative*, m.p. 141°. (The nitration should be carried out in a fume cupboard as the reaction is violent and copious fumes of $NO_2$ are evolved.)

Into a 100-c.c. beaker pour 4 c.c. of fuming $HNO_3$ and add rapidly 1 g. of O.S. When the violent reaction has ceased, heat on a water bath for 10 min. Cool, add 5 c.c. water and stir until the oil solidifies. Filter off the solid and wash it well with water. Dissolve the solid in a small quantity of acetone and filter. Precipitate the nitro compound by the addition of alcohol, filter and wash the solid with alcohol. Redissolve the solid in acetone and precipitate again with alcohol, etc. Dry the solid and determine the m.p.

37° β-Naphthyl ethyl ether.



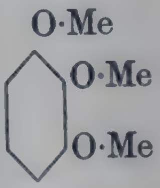
Powerful floral odour.

B.p. 282°.

Picrate, m.p. 104° (see page 143).

% ethoxyl radical = 26·1.

47° Pyrogallol trimethyl ether,



B.p. 235°.

% methoxyl radical = 55·4.

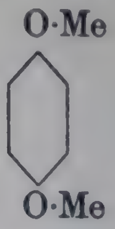
52° Dibenzyl. $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$. B.p. 284°.

*Oxidation to benzoic acid*, m.p. 121° :—

In a 100-c.c. wide-mouthed flask place 2½ g. solid $KMnO_4$, 40 c.c. water, 5 drops aq. NaOH, ½ g. of O.S. and two or three pieces of porous pot. Fit the flask with a reflux condenser, heat the contents to boiling and continue boiling fairly rapidly for 2 hr. Cool, then pass $SO_2$ until any purple colour and the brown ppt. have disappeared. Heat the liquid to boiling, filter from unchanged hydrocarbon, cool well and shake.

Filter off the solid and wash it with cold water, crystallise from water, dry, and determine the m.p.

M.p.

55° Quinol dimethyl ether. 

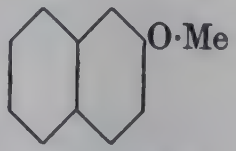
B.p. 212°.

% methoxyl radical = 44·9.

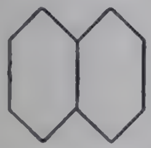
70° Diphenyl. $C_6H_5{\cdot}C_6H_5$. B.p. 254°.

*Preparation of pp′-dibromo-derivative*, m.p. 169° :—

In a 100-c.c. beaker place $\frac{1}{2}$ g. of O.S. and an amount of iodine roughly equal in bulk to a half-pea. Add a soln. of 1 c.c. Br in 4 c.c. $CCl_4$. Allow to stand 10 min., then evaporate to dryness on a water bath. Add 10 c.c. boiling aq. NaOH and stir, in order to remove as much iodine as possible. Dilute with 10 c.c. water, filter and wash the solid with water. Crystallise the solid from acetone, dry, and determine the m.p.

72° β-Naphthyl methyl ether. (Nerolin.) 

Powerful odour of orange blossom. B.p. 274°.
Picrate, m.p. 118° (see page 143).
% methoxyl radical = 19·6.

80° Naphthalene.  Characteristic odour. B.p. 218°.

*Preparation of picrate (yellow)*, m.p. 149° :—

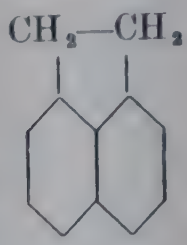
Dissolve $\frac{1}{8}$–$\frac{1}{4}$-in. layer of powdered O.S. in a t.t. in 1 c.c. cold benzene. Add 2 c.c. of a saturated soln. of picric acid in benzene and shake. Filter off the ppt. and carefully wash it with a few drops of cold benzene. Press the ppt. between filter paper, dry over a small flame, and determine the m.p.

92° Triphenylmethane. $(C_6H_5)_3CH$.

In a dry t.t. place 0·1 g. of O.S. and add 2 c.c. fuming $HNO_3$; allow to stand 5 min. Nearly fill the tube with cold water and shake. Filter off the pptd. trinitro compound and wash it with water. Transfer the ppt. to a t.t. and dissolve it in 10 c.c. glacial acetic acid. Add Zn dust until the deep red colour, which is formed at first, disappears,

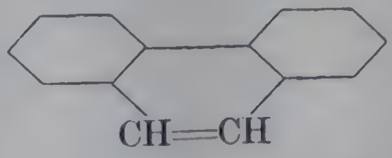
M.p. then filter. To 2 c.c. of the yellow filtrate add 2 R.G. of $PbO_2$ and shake,
—intense red colour, due to the formation of pararosaniline.

95° **Acenaphthene.**



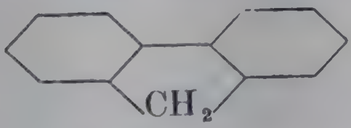
Picrate (orange), m.p. 161°. (For preparation see under "Naphthalene," page 123.)

100° **Phenanthrene.**



Picrate (yellow), m.p. 143°. (For preparation see under "Naphthalene." After mixing the two solns., heat just to boiling, cool and shake.)

113° **Fluorene.**



*Oxidation to the ketone, fluorenone* (yellow), identified by conversion to its phenylhydrazone, m.p. 151°.

In a 100-c.c. wide-mouthed flask place 1 g. of O.S., 3g. sodium dichromate and 5 c.c. glacial acetic acid. Fit the flask with a reflux condenser, heat the contents of the flask to boiling and continue boiling gently, with periodic shaking round, for $\frac{1}{2}$ hr.

Add through the condenser 50 c.c. of boiling water. Transfer the contents of the flask to a 500-c.c. distilling flask, make up the volume to about 300 c.c. with water and add 2 or 3 pieces of porous pot. Connect the flask to a condenser and boil the contents vigorously. Filter off the yellow fluorenone which passes over with the steam, and prepare its phenylhydrazone in the manner described under "O.S. solid," (page 66).

Crystallise the phenylhydrazone from alcohol (the derivative is sparingly soluble in alcohol, whereas fluorenone is readily soluble) dry, and determine the m.p

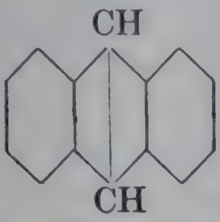
M.p.

125° Stilbene. $C_6H_5 \cdot CH{:}CH \cdot C_6H_5$.

(*a*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 5 c.c. dichromate mixture, heat to boiling and continue boiling for $\frac{1}{2}$ min.,
—bitter almond odour of benzaldehyde.

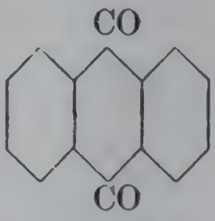
(*b*) Pour 5 c.c. Br water into each of two t.t.s. To one add the equivalent of $\frac{1}{8}$-in. layer of O.S. in a t.t. Stand both tubes in boiling water for 1 min., then take them out and shake vigorously. It will be found that the liquid in the tube containing the hydrocarbon has become colourless (owing to the presence of a double bond in the molecule of the substance), whereas in the blank test the colour of the bromine persists.

216° Anthracene.



(*a*) Add 2 R.G. of O.S. to 2 c.c. of a saturated soln. of picric acid in benzene and shake,
—deep red soln., due to the formation of a red picrate.

(*b*) *Oxidation to Anthraquinone.*

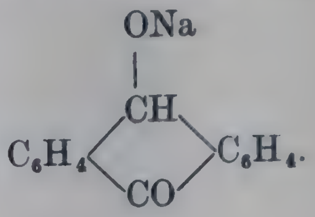


Weigh out in a 100-c.c. wide-mouthed flask 1 g. of $CrO_3$ and add a mixture of 1 c.c. water and 9 c.c. glacial acetic acid. Heat until the $CrO_3$ has dissolved; cool.

Add $\frac{1}{2}$ g. of O.S., fit the flask with a reflux condenser and heat the contents to boiling. (If the mixture froths up, remove the flame for a moment.) Continue boiling gently for 10 min., shaking the flask round periodically. Allow to cool somewhat, then add 50 c.c. water. Filter, and wash the solid with water until it is a clean yellow colour. Apply the following test for anthraquinone :—

In a t.t. place 2 R.G. of the yellow solid and an equal bulk of Zn dust. Add 5 c.c. aq. NaOH, heat to boiling and continue boiling for ½ min., —deep red colour.

Filter while hot into a t.t. and shake, —red colour rapidly disappears, owing to oxidation by the air, and a flocculent pale yellow ppt. of anthraquinone separates. The phenomena described may be repeated by adding Zn dust and boiling, etc. The red colour is due to the Na salt of oxanthranol,



## Determination of the Percentage of Methoxyl or Ethoxyl Radical in Methyl or Ethyl Ethers

### Perkin's modification of Zeisel's method.

The method depends on the fact that when a compound which contains methoxyl or ethoxyl groups is heated with hydriodic acid, the methyl or ethyl groups are converted into methyl or ethyl iodide, which when passed into an aqueous alcoholic soln. of silver nitrate, is decomposed with the formation of silver iodide. From the weight of silver iodide produced the percentage of methoxyl or ethoxyl radical is calculated.

*Reagents employed.*

*Hydriodic acid.* The constant boiling mixture is required, b.p. 127° and *d.* 1·70, containing 57% of HI. Such an acid, for use in Zeisel estimations, may be purchased.

*Aqueous alcoholic silver nitrate solution.* Dissolve 2 g. $AgNO_3$ in 5 c.c. distilled water and add 45 c.c. absolute alcohol. The soln. must be kept in the dark, and if not clear, the required quantity should be filtered through a dry filter paper into the absorption flasks.

*Carbon dioxide.* This may be obtained from a Kipp's apparatus, the gas being washed free from traces of HCl and any $H_2S$ (arising from impurities in the marble) by passing through a dilute soln. of $AgNO_3$, and then dried by passing through conc. $H_2SO_4$.

*Apparatus.*

The apparatus used is illustrated in Fig. 12. The long neck of the special Zeisel flask A acts as an air condenser and keeps back the hydriodic acid and any iodine present. It should be noted that the end of the connecting tube in the first flask (containing 20 c.c. of the $AgNO_3$ soln.) terminates just above the surface of the liquid, while that in the second flask (containing 15 c.c. of $AgNO_3$ soln.) dips well below the liquid.

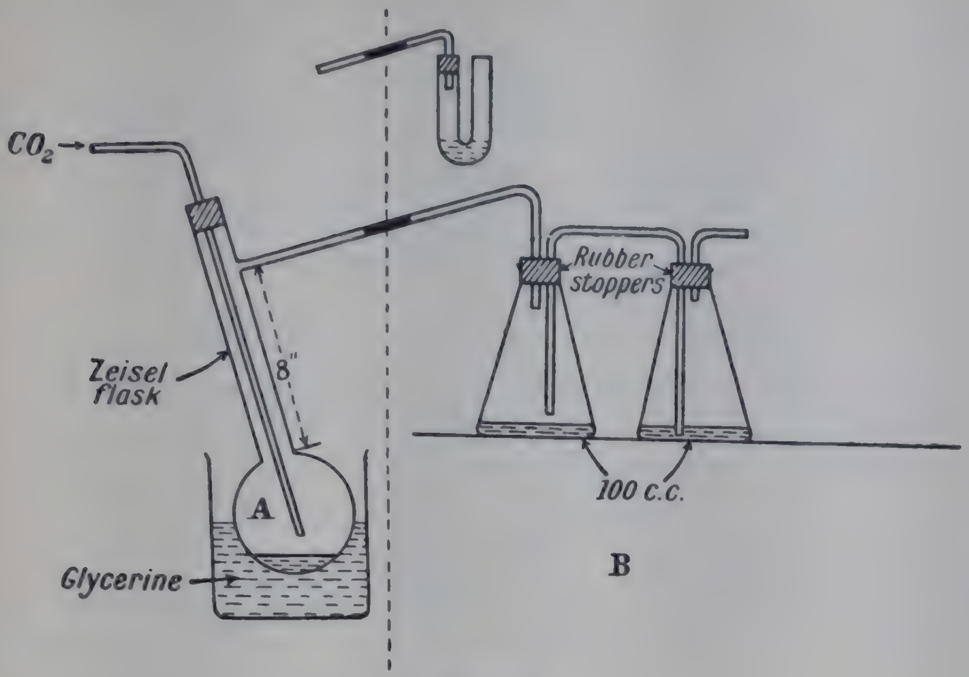


FIG. 12.

*Procedure:—*

Remove the cork and tube from **A**, and by means of a thistle funnel, the end of which reaches well into the bulb, introduce 15 c.c. of the hydriodic acid into the flask. Allow the stem of the funnel to drain and then carefully remove the funnel so that no drops of acid are left on the neck of the flask. Add a few pieces of porous pot to the contents of the flask, then replace the cork and tube so that the end of the tube is just above the acid.

Attach to the side-tube of the distilling flask a U-tube containing a few c.c. of the $AgNO_3$ soln. Raise the temperature of the glycerine bath to 130° and pass a slow current of $CO_2$ through the apparatus until the issuing gas does not give a turbidity with a quantity of clear $AgNO_3$ soln. (This is to remove any volatile impurities from the hydriodic acid.) Allow the apparatus to cool, disconnect the U-tube and replace it by the absorption apparatus **B**.

Weigh out accurately in a small glass tube about 0·3 g. of the ether, remove the cork carrying the $CO_2$ tube and slide the tube containing the ether down into the acid (if necessary push it down with the $CO_2$ tube). Firmly replace the cork and $CO_2$ tube, pass a slow current of $CO_2$ through the apparatus (about 2 bubbles per second through the $H_2SO_4$ wash-bottle), and heat the glycerine to 130°–140°. A white deposit (a compound of silver iodide and nitrate) soon begins to form on the surface of the liquid in the first flask and gradually settles to the bottom, but usually only a trace appears in the second flask.

After about 20 min. raise the temperature of the glycerine until the hydriodic acid boils gently, but not so vigorously as to cause distillation of the acid into the side-tube of the flask. Continue heating for 40 min. then disconnect the flasks and substitute for them the cleaned U-tube, containing a few c.c. of the $AgNO_3$ soln.

Heat for a further period of 20 min., and if no appreciable quantity of ppt. forms, the distillation of the methyl or ethyl iodide may be considered complete; otherwise pour the soln. into one of the flasks, place a fresh quantity in the U-tube, and repeat the process until the formation of ppt. ceases.

To 50 c.c. distilled water contained in a 250-c.c. beaker add 10 c.c. dil. $HNO_3$ and heat to boiling. Gradually add the contents of both flasks and rinse out the flasks, the connecting tube and the U-tube with hot distilled water into the beaker. Continue boiling for some time in order to drive off the alcohol, and to decompose completely the white, somewhat stable, double salt of silver iodide and silver nitrate which has been formed by the interaction of the methyl or ethyl iodide and the alcoholic $AgNO_3$ soln.

Add boiling distilled water, if necessary, to prevent the volume becoming less than about 50 c.c. and break up any lumps of ppt. by means of a glass rod. Allow the soln. to stand in the dark for an hour, then filter off the ppt. of AgI into a tared Gooch or sintered glass crucible, wash, dry at 100°, and weigh.

234·8 g. of AgI correspond to 31·02 g. of $O—CH_3$, or 45·04 g. of $O—C_2H_5$.

EXAMPLE:—0·3150 g. of a methyl ether gave 0·4680 g. AgI.

$$\% \text{ methoxyl radical} = \frac{31{\cdot}02 \times 0{\cdot}468 \times 100}{234{\cdot}8 \times 0{\cdot}3150} = 19{\cdot}6.$$ The results obtained with ethoxy compounds are generally somewhat low.

## ADDITIONAL COMPOUNDS CONTAINING C and H, OR C, H, AND O

NOTES:

(1) Unsaturated compounds may be detected by the following test:—

To $\frac{1}{8}$-in. layer in a t.t. of a soln. of Br in $CCl_4$ add one or two drops of O.S. and shake—brown colour rapidly disappears. Pour the contents slowly out of the tube,—no copious evolution of HBr fumes, indicating that addition and not substitution has occurred.

(2) For further properties and derivatives a more comprehensive work should be consulted.

(3) The class of the substance, if not a hydrocarbon, is stated.

*Liquids.*

**Float on water.**

| B.p. | |
|---|---|
| 30° | *iso*-Pentane.. $(CH_3)_2CH{\cdot}CH_2{\cdot}CH_3$. Petrol-like odour. |
| 35° | Diethyl ether. $(C_2H_5)_2O$. |
| 36° | *n*-Pentane. $CH_3{\cdot}[CH_2]_3{\cdot}CH_3$. Petrol-like odour. (Standard pentane, boiling range 25°–40°.) |
| 69° | *n*-Hexane. $CH_3{\cdot}[CH_2]_4{\cdot}CH_3$. Petrol-like odour. |
| 69° | Di-*iso*propyl ether. $(CH_3)_2CH{\cdot}O{\cdot}CH(CH_3)_2$. |
| 90° | Di-*n*-propyl ether. $(CH_3{\cdot}CH_2{\cdot}CH_2)_2O$. |
| 98° | *n*-Heptane. $CH_3{\cdot}[CH_2]_5{\cdot}CH_3$. Petrol-like odour. |
| 125° | *n*-Octane. $CH_3{\cdot}[CH_2]_6{\cdot}CH_3$. Petrol-like odour. |
| 146° | Styrene. $C_6H_5{\cdot}CH{:}CH_2$. Unsaturated. |
| 155° | Pinene. $C_{10}H_{16}$. Odour of turpentine. Unsaturated. |
| 164° | Mesitylene. $C_6H_3(CH_3)_3{\cdot}(1{:}3{:}5)$. |
| 176° | Cineole. $C_{10}H_{18}O$. Odour of eucalyptus. (Ether.) |
| 176° | Limonene. $C_{10}H_{16}$. Odour of lemon. Unsaturated. |
| 182° | Indene. $C_9H_8$. Unsaturated. |
| 192° | Decahydronaphthalene. $C_{10}H_{18}$. |
| 206° | Tetrahydronaphthalene. $C_{10}H_{12}$. |

**Sink in water.**

| | |
|---|---|
| 240° | α-Methylnaphthalene. $C_{10}H_7{\cdot}CH_3$. Picrate, m.p. 141°. |
| 295° | Dibenzyl ether. $(C_6H_5{\cdot}CH_2)_2O$. |

*Solids.*

| M.p. | |
|---|---|
| 32° | β-Methylnaphthalene. $C_{10}H_7{\cdot}CH_3$. Picrate, m.p. 115°. |
| 33° | Cinnamyl alcohol. $C_6H_5{\cdot}CH{=}CH{\cdot}CH_2OH$. See page 38. |
| 42° | *l*-Menthol. $C_{10}H_{19}OH$. Odour of peppermint. (Saturated alcohol.) |
| 48° | Cetyl alcohol. $CH_3{\cdot}[CH_2]_{14}{\cdot}CH_2OH$. |
| 51° | *l*-Camphene. $C_{10}H_{16}$. Unsaturated. |
| 68° | Diphenylcarbinol. $(C_6H_5)_2CH{\cdot}OH$. (Secondary alcohol.) |
| 116° | Terpin hydrate. $C_{10}H_{20}O_2$, $H_2O$. |
| 162° | Triphenylcarbinol. $(C_6H_5)_3{\cdot}C{\cdot}OH$. (Tertiary alcohol.) |
| 203° | *d*-Borneol. $C_{10}H_{17}OH$. Odour like camphor. (Secondary alcohol.) |

# SCHEME II

## Compounds containing Cl, Br, or I.

Follow the appropriate procedure either under "O.S. liquid" (below) or under "O.S. solid" (page 132).

*O.S. liquid.*

Apply the following tests in the order given.

(1) To 3 c.c. of distilled water in a t.t. add one drop of O.S., heat to boiling; continue boiling with shaking for 1 min., then cool. To the clear soln. (if necessary obtained by filtration) add 2 c.c. of dil. $HNO_3$ and 1 c.c. of aq. $AgNO_3$. If a definite ppt. of Ag halide is obtained (ignore a slight milkiness) see "Acid halides, etc." (page 150), otherwise apply Test 2.

(2) To $\frac{1}{8}$-in. layer of 2 : 4-dinitrophenylhydrazine in a dry t.t. add $2\frac{1}{2}$ c.c. of alcohol, then add $\frac{1}{2}$ c.c. of conc. $H_2SO_4$. Warm and shake in order to dissolve all the solid. To the soln. add $\frac{1}{2}$ c.c. of O.S., shake and allow to stand for 5 min. unless a ppt. forms in a shorter period of time. Finally cool and shake the contents of the t.t. If a ppt. is obtained, retain it and see "Halogen-aldehydes and halogen-ketones" (page 138), or if there is no ppt. apply Test 3.

(It is necessary to apply this test before Test 3 as chlorobenzaldehydes dissolve somewhat in aq. NaOH and are re-precipitated from the alkaline soln. by HCl.)

(3) To 5 drops of O.S. in a t.t. add 3 c.c. of approx. 2N. NaOH, close the mouth of the tube and shake vigorously for 1 min. If any O.S. has remained undissolved add 3 c.c. of water, then shake and filter the contents of the t.t. Acidify the soln. or filtrate with conc. HCl. If a white emulsion or an oil is obtained, see "Halogen-phenols" (page 136), otherwise apply Test 4. (No account is taken here of halogen-substituted higher aliphatic acids, which, if sparingly soluble in water, would give a positive result in this test.)

(4) To 2 c.c. of alcohol add one drop of O.S. and 10 drops of approx. $\frac{N}{10}$NaOH, shake round and then add a drop of phenolphthalein

soln. If the soln. remains colourless see "Aliphatic halogen-acids" (page 133) or if a red colour is produced apply Test 5.

(5) To 1 c.c. of acetyl chloride in a *dry* t.t. add about ½ c.c. of O.S. If within 2 min. a vigorous reaction occurs (i.e. bubbles are freely evolved) with evolution of HCl fumes, see "Halogen-alcohols" (page 137), otherwise apply Test 6.

(6) In a 100-c.c. wide-mouthed flask place 2 g. of solid KOH and 10 c.c. of alcohol and heat under a reflux condenser until all the KOH has dissolved. Pour 2 c.c. of the soln. into a t.t. for use as a blank test. To the remaining soln. in the flask add ½ c.c. of O.S. and heat to boiling under the condenser. If a considerable ppt. separates, no further boiling is necessary, otherwise continue boiling for 10 min. Cool, acidify with dil. $HNO_3$, *cool well and shake*, then filter. Also acidify the 2 c.c. of alcoholic KOH in the t.t. with dil. $HNO_3$. To 2 c.c. of each acidified soln. add 1 c.c. of aq. $AgNO_3$.

If there is obtained

(*a*) a ppt. of Ag halide greater than that obtained in the blank test see "Aliphatic halogen-hydrocarbons, etc." (page 140).

(*b*) no greater ppt. of Ag halide than that obtained in the blank test proceed as under (*b*), page 99, in order to ascertain if O.S. is an ester of an aromatic halogen acid. If O.S. is not an ester, see "Aromatic halogen-hydrocarbons" (page 146).

### *O.S. solid.*

Follow the appropriate procedure either on page 133 or below, according to whether a metal is present or not.

### No metal present.

To a measured ⅛-in. layer of powdered O.S. in a dry ⅝-in. t.t. add *5 c.c.* of distilled water, heat to boiling with shaking, then cool well and shake. If O.S. is completely in solution, apply Test 1 (below) or if it is not completely in solution proceed as under (1), page 131, using R.G. of O.S. If no ppt. of Ag halide is obtained, apply Test 3 (below).

(1) To 2 c.c. of the aq. soln. of O.S. add a drop of aq. $FeCl_3$. If a blue, violet, or green colour is observed see "Halogen-phenols" (page 136); if none of these colours is obtained then to 2 c.c. of dil. $NH_4OH$ add R.G. of O.S. and shake for 1 min. If a deep brown or deep red colour is observed see "Halogen-phenols" (page 136), otherwise to a soln. of R.G. of O.S. in 2 c.c. of water add 5 drops of approx. $\frac{N}{10}$ NaOH, shake and then add a drop of phenolphthalein soln. If the soln. remains

colourless see "Aliphatic halogen-acids" (page 133) or if a red colour is produced apply Test 2.

(2) To ⅛-in. layer of O.S. in a t.t. add 2 c.c. of approx. 2N. NaOH, heat to boiling, continue boiling gently for 1 min., then cool. Add a drop of phenolphthalein soln., then add dil. HCl until the soln. *just* becomes colourless. Now add 1 c.c. of aq. $HgCl_2$. heat to boiling, continue boiling for 1 min., then cool and shake, A white ppt. of $Hg_2Cl_2$ (due to the reduction of the $HgCl_2$ by a formate produced by hydrolysis) suggests that O.S. is a hydrate or alcoholate of a halogen-aldehyde. See page 139.

(3) To ⅛-in. layer of O.S. in a dry t.t. add 3 c.c. of alcohol, heat just to boiling, then cool and shake; filter if any solid is present. Using this alcoholic soln. instead of the ½ c.c. of O.S. proceed as in Test 2 (page 131). If a ppt. is obtained retain it, and see "Halogen-aldehydes and halogen-ketones" (page 138), otherwise apply Test 4.

(4) To ⅛-in. layer of O.S. in a t.t. add 3 c.c. of approx. 2N. NaOH, close the mouth of the tube and shake vigorously for 1 min. If any O.S. has remained undissolved add 3 c.c. of water, then shake and filter the contents of the t.t. Acidify the soln. or filtrate with conc. HCl. If a ppt. or a white emulsion is obtained, see "Aromatic halogen-acids and halogen-phenols" (page 135), otherwise apply Test 5 unless O.S. has a camphor-like odour, in which case see first "Chlorbutol" (page 138).

(5) Proceed as in Test 6 (page 132) using the equivalent of ⅛-in. layer in a t.t. of O.S.

**Metal present.**

Only alkali salts of halogen-acids are here considered.

*Procedure:—*

Prepare about 5 c.c. of a cold, concentrated soln. of O.S. and acidify with conc. HCl.

If there is obtained

(*a*) no ppt., proceed as indicated under "Aliphatic halogen-acids" (page 133).

(*b*) a ppt., filter it off, wash it with cold water, dry, and proceed as indicated under "Aromatic halogen-acids" (page 135).

## *HALOGEN-CARBOXYLIC ACIDS*

### Aliphatic halogen-acids.

The halogen-substituted acetic acids included in this subsection possess a sharp odour, are deliquescent if solid, and have a blistering action on the skin.

***O.S. liquid.***

*Chloro-acids.*

Apply the following test for "Dichloroacetic acid" $CHCl_2{\cdot}COOH$, b.p. 190°. Into a small flask pour ½ c.c. of O.S. and 10 c.c. of 20% aq. KOH, heat to boiling and continue boiling gently for 5 min. (Soln. becomes yellow). Acidify 2 c.c. of the soln. with glacial acetic acid, heat to boiling and add 2–3 drops aq. $CaCl_2$, —immediate white ppt. (Ca oxalate, due to the formation of oxalic acid).

Confirm the identity of O.S. by preparation of the aniline salt, m.p. 122° as follows :—Mix intimately in a porcelain dish 1 c.c. each of O.S. and freshly distilled aniline. When the mixture has become solid, triturate with 3 c.c. ether. Filter, wash the salt carefully with ether until white, dry, and determine the m.p.

***O.S. solid.***

*Chloro-acids.*

Proceed as indicated under "Trichloroacetic acid."

If negative results are obtained follow the procedure under "Chloroacetic acid."

M.p.

55° Trichloroacetic acid. $CCl_3{\cdot}COOH$.

Apply the tests under "Chloroform" (page 140) using R.G. of O.S., when similar results will be obtained owing to chloroform being first formed.

63° Chloroacetic acid. $CH_2Cl{\cdot}COOH$.

(*a*) In a boiling-tube place the equivalent of ⅛-in. layer of O.S. in a t.t. and add 10 c.c. aq. NaOH. Heat to boiling and continue boiling for 1 min. Add the equivalent of ⅛-in. layer in a t.t. of solid $KMnO_4$ and shake until the green colour has disappeared, then filter. To 2 c.c. of the filtrate add 1 c.c. glacial acetic acid, heat to boiling and add 2–3 drops aq. $CaCl_2$,
—immediate white ppt. (Ca oxalate, due to oxalic acid formed by oxidation of the glycollic acid produced by hydrolysis).

(*b*) *Preparation of phenoxyacetic acid,*

$$C_6H_5O{\cdot}CH_2{\cdot}COOH,$$

m.p. 96° :—

In a 100-c.c. wide-mouthed flask place 1 g. of O.S., 1 g. of phenol, 1½ g. KOH and 10 c.c. water. Fit the flask with a cork and reflux condenser, heat the contents to boiling and continue boiling for 5 min. Cool, acidify with conc. HCl, shake and cool until solid separates. Filter, wash the solid with cold water, crystallise it from water, dry, and determine the m.p.

*Bromo-acids.*

M.p.

50° Bromoacetic acid. $CH_2Br{\cdot}COOH$.

Follow the procedure under "Chloroacetic acid" (page 134) when similar results will be obtained.

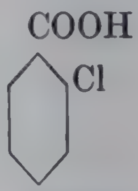
**Aromatic halogen-acids and halogen-phenols.**

Determine the m.p. of O.S. (if below 100° see "Halogen-phenols," (page 136), and refer to the appropriate list of m.p.s of acids. Method 1 (page 81) should be used for the determination of the equivalent weight. For derivatives see page 80.

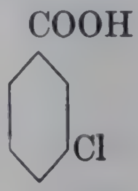
*Chloro-acids.* *Equiv. wt.*

M.P.

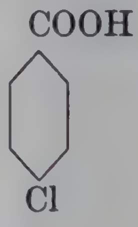
140° *o*-Chlorobenzoic acid.
Amide, m.p. 142°.
*p*-Nitrobenzyl ester, m.p. 106°.



153° *m*-Chlorobenzoic acid.
Amide, m.p. 134°.
*p*-Nitrobenzyl ester, m.p. 110°.

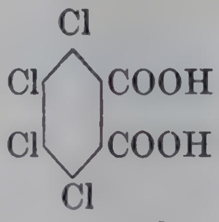


236° *p*-Chlorobenzoic acid.
Amide, m.p. 179°.
*p*-Nitrobenzyl ester, m.p. 129°.



156·5

250° decomp. Tetrachlorophthalic acid.
*p*-Nitrobenzyl ester, m.p. 180°.

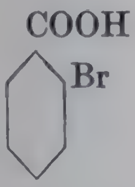


151·9

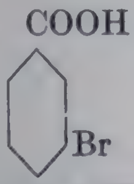
*Bromo-acids* *Equiv. wt.*

M.p.

147° *o*-Bromobenzoic acid.
Amide, m.p. 157°.
*p*-Nitrobenzyl ester, m.p. 110°.



155° *m*-Bromobenzoic acid.
Amide, m.p. 155°.
*p*-Nitrobenzyl ester, m.p. 105°.

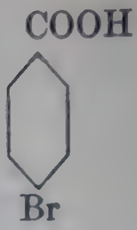


200·9

195° Dibromocinnamic acid. $C_6H_5{\cdot}CHBr{\cdot}CHBr{\cdot}COOH$. 307·9

M.p.

251° *p*-Bromobenzoic acid.
Amide, m.p. 189°.
*p*-Nitrobenzyl ester, m.p. 139°.



200·9

## *HALOGEN-PHENOLS*

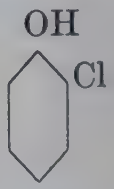
*Procedure for the identification of O.S.* :—

Determine the b.p. if liquid, or the m.p. if solid, and refer to the following list of b.p.s or m.p.s, taking into account the particular halogen present. If one of these b.p.s or m.p.s is identical with, or near to, that of O.S., confirm the identity of O.S. by preparing and determining the m.p. of one of the derivatives there indicated. The method of preparation of acetates is described on page 52, of benzoates on page 52, and of methyl ethers on page 162. Bromo derivatives should be prepared in the manner described for *m*-cresol, page 53.

***Liquids.*** (See also solids of low m.p.)

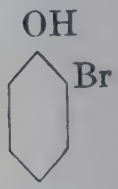
B.p.

175° *o*-Chlorophenol.



Bromo derivative, m.p. 73°.
$FeCl_3$: violet (water)

194° *o*-Bromophenol.

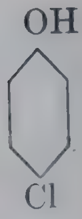


Bromo derivative, m.p. 93°.
$FeCl_3$: violet (water).

***Solids.***

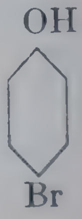
M.p.

37° *p*-Chlorophenol.
B.p. 217°.



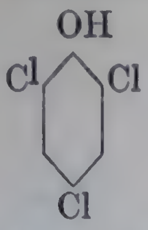
Benzoate, m.p. 88°.
$FeCl_3$: violet (water)

63° *p*-Bromophenol.
B.p. 235°.



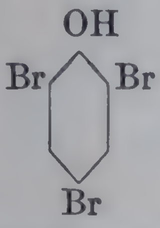
Benzoate, m.p. 104°.
$FeCl_3$: violet (water).

M.p.



67° *sym*-Trichlorophenol. FeCl$_3$: no colour.

Benzoate, m.p. 70°, Methyl ether, m.p. 60°.



93° *sym*-Tribromophenol. FeCl$_3$: no colour.

Acetate, m.p. 82° (crystallise from alcohol). Methyl ether, m.p. 87°.

## *HALOGEN-ALCOHOLS*

***O.S. liquid containing Cl.***

*Procedure for identification.*

Determine the b.p. and refer to the following list of b.p.s. If one of these b.p.s is identical with, or near to, that of O.S., confirm the identity of O.S. by applying to it any tests given, and by preparing and determining the m.p. of the derivative there indicated.

B.p.

127° Ethylene chlorhydrin. $CH_2OH{\cdot}CH_2Cl$. Miscible with water.

(*a*) Pour into a boiling tube ½ c.c. of O.S. and 10 c.c. aq. NaOH, heat to boiling and continue boiling for 1 min. Add an amount of solid $KMnO_4$ equivalent to ⅛-in. layer in a t.t. and shake until the green colour disappears. Filter, acidify 2 c.c. of the filtrate with glacial acetic acid, heat to boiling and add 2–3 drops of aq. $CaCl_2$,
—white ppt. (Ca oxalate, due to oxalic acid having been formed by the oxidation of the ethylene glycol produced by hydrolysis.)

(*b*) *Preparation of ethylene glycol dibenzoate*, m.p. 73°:—
Into a 100-c.c. conical flask pour 2 c.c. of O.S. and 20 c.c. aq. NaOH, heat to boiling and continue boiling gently for 5 min. Cool, add 2 c.c. benzoyl chloride and 20 c.c. aq. NaOH. Cork the flask and shake until solid separates, then shake for a

B.p. further period of 10 min. Filter, wash the solid with cold water, crystallise it from a small quantity of alcohol, dry, and determine the m.p.

176° Glycerol α-Dichlorhydrin. $CH_2Cl{\cdot}CH(OH){\cdot}CH_2Cl.$
182° Glycerol β-Dichlorhydrin. $CH_2Cl{\cdot}CHCl{\cdot}CH_2OH.$

*Preparation of glycerol diphenyl ether*, m.p. 81°. See page 144.

***O.S. solid, containing Cl.***

Chlorbutol (Chloretone, Trichloro-tertiary butyl alcohol). $CCl_3{\cdot}C(CH_3)_2{\cdot}OH$. Camphor-like odour. M.p. about 80°, if anhydrous 96°. Reduces Tollen's reagent (see below under "Chloral," (*b*).

In a 100-c.c. wide-mouthed flask place 1 g. of O.S., 20 c.c. aq. NaOH and some porous pot. Connect the flask to a water condenser, use a t.t. as the receiver, and distil until 6–7 c.c. of distillate is obtained. Filter the distillate in order to remove unchanged O.S. and apply to the filtrate the following tests for acetone :—

(*a*) To 2 c.c. add an equal volume of ½% aq. sodium nitroprusside and 2 drops aq. NaOH,
—wine-red colour develops, turned violet-red on acidifying with acetic acid.

(*b*) To 2 c.c. add an equal volume of iodine soln., then add aq. NaOH, drop by drop, until the deep brown colour just disappears,
—immediate pale yellow ppt. of iodoform with characteristic odour.

## *HALOGEN-ALDEHYDES AND HALOGEN-KETONES*

These will have been indicated by Test 2 (page 131). For other aldehydes and ketones see page 152.

B.p.
98° Chloral. $CCl_3{\cdot}CHO$. Pungent odour, somewhat resembling that of cucumber.

(*a*) To ⅛-in. layer of O.S. in a t.t. add 2 c.c. aq. NaOH, heat to boiling, continue boiling for ½ min., then cool. Add a drop of phenolphthalein soln., then add dil. HCl until the soln. just becomes colourless. Add 1 c.c. aq. $HgCl_2$, heat to boiling and continue boiling for ½ min.; cool,
—white ppt. ($Hg_2Cl_2$, due to Na formate, produced together with chloroform by the action of NaOH on O.S.)

(*b*) Add one drop of O.S. to Tollen's reagent (1 c.c. aq. $AgNO_3$, 1 c.c. aq. NaOH; add dil. $NH_4OH$,

B.p. drop by drop, until a clear, colourless soln. is just obtained),
—immediate reduction (dark grey ppt.).

118° Chloroacetone. $CH_2Cl\cdot CO\cdot CH_3$. Lachrymatory.
In a t.t. place 3 R.G. of $\beta$-naphthol and add 2 c.c. aq. NaOH and one drop of O.S.,
—violet-red colour appears in a few sec.
2:4-Dinitrophenylhydrazone (prepare as in Test 2, page 131, but using cold solutions, and merely washing with cold alcohol), m.p. 109°.

45° *sym*-Dichloroacetone. $CH_2Cl.\cdot CO\cdot CH_2Cl$. B.p. 173°.
Sparingly soluble in water. Irritating odour.
2:4-Dinitrophenylhydrazone (prepare as in Test 3, page 133, using cold solutions, and merely washing with cold alcohol), m.p. 128°.

## *HYDRATES AND ALCOHOLATES OF HALOGEN-ALDEHYDES*

(*Chloral hydrate, chloral alcoholate, butyl chloral hydrate*)

These compounds will have been indicated by the production of a formate on boiling with aq. NaOH. (Test 2, page 133.)

*Procedure for the identification of O.S.*

In a t.t. place 3 R.G. of resorcinol, add 2 c.c aq. NaOH and R.G. of O.S. and heat to boiling.

If there is obtained

(*a*) no red colour, determine the m.p. of O.S. M.p. 78° indicates that O.S. is butyl chloral hydrate $CH_3\cdot CHCl\cdot CCl_2\cdot CH(OH)_2$ (odour resembling that of stale fruit).

(*b*) a red colour, appearing violet-red on shaking, either chloral hydrate $CCl_3\cdot CH(OH)_2$ (m.p. 57°. Odour somewhat resembling that of cucumber) or chloral alcoholate $CCl_3\cdot CH(OH)\cdot O\ Et$ (m.p. 56°. Somewhat fruity odour) is indicated. To distinguish proceed as follows :—

In a 100-c.c. wide-mouthed flask place 1 g. of O.S., 20 c.c. aq. NaOH and some porous pot. Connect the flask to a water condenser, use a t.t. as receiver, and distil until 6–7 c.c. of distillate is obtained. To 2 c.c. of distillate add 2 c.c. iodine soln., then add aq. NaOH, drop by drop, until the deep brown colour just disappears. Stand the t.t. in water at 60° for 1 min., then cool.

A pale yellow ppt. of iodoform, with characteristic odour, indicates that O.S. is chloral alcoholate. With chloral hydrate a clear soln. is obtained.

## *ALIPHATIC HALOGEN-HYDROCARBONS, AROMATIC HYDROCARBONS WITH HALOGEN IN THE SIDE-CHAIN, HALOGEN ETHERS, AND HALOGEN ESTERS*

*Procedure for the identification of O.S.*

Determine the b.p. if liquid, or the m.p. if solid, and refer to the list of b.p.s or m.p.s in the appropriate subsection, according to whether O.S. contains Cl, Br (page 141), or I (page 142). If one of these b.p.s or m.p.s is identical with, or near to, that of O.S., confirm the identity of O.S. by applying to it the tests given, or by preparing and determining the m.p. of the derivative there indicated. The methods of preparation of derivatives are given on page 143. If O.S. is not found to be identical with one of the compounds in the following lists, see " Additional aliphatic halogen-hydrocarbons, etc.," (page 144).

### Chloro compounds.

#### *Liquids.*

B.p.

61° Chloroform. $CHCl_3$.

(*a*) In a t.t. place 3 R.G. of resorcinol and add 2 c.c. aq. NaOH and one drop of O.S.; heat to boiling,
—red soln., appearing violet red on shaking.

(*b*) To 2 c.c. alcohol in a t.t. add one drop of aniline, one drop of O.S. and 3 R.G. of solid NaOH. Heat to boiling in a fume cupboard and continue boiling for 15 sec.
—strong obnoxious odour of phenyl isocyanide (carbylamine). Immediately the odour is detected, cool and add excess of conc. HCl in order to destroy the isocyanide.

77° Carbon tetrachloride. $CCl_4$.

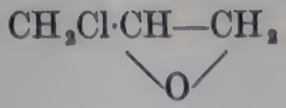
(*a*) Apply Test (*b*) under " Chloroform," when little or no obnoxious odour of phenyl isocyanide will be obtained.

(*b*) To 2 c.c. alcohol in a t.t. add one drop of O.S., 5 drops of dil. HCl and 3 R.G. of zinc dust. Shake for 2 min., then add one drop of aniline and 5 R.G. of solid NaOH. Heat to boiling in a fume cupboard and continue boiling for 15 sec.,
—strong obnoxious odour of phenyl isocyanide.

Immediately the odour is detected, cool and add an excess of conc. HCl in order to destroy the isocyanide.

B.p.

117° Epichlorhydrin.



$CH_2Cl{\cdot}CH{-}CH_2$ (with $O$ bridging the two CH groups)

Glycerol diphenyl ether, m.p. 81°.

130° Methyl chloroacetate. $CH_2Cl{\cdot}COO\ Me.$

144° Ethyl chloroacetate. $CH_2Cl{\cdot}COO\ Et.$

(*a*) Identify the alkyl radical in the manner described under "Esters of carboxylic acids" (page 100). Use half quantities for the hydrolysis, which will be complete in 10 min.

(*b*) Identify the acid constituent by the preparation of chloroacetamide, m.p. 119°, as follows:—To 2 c.c. of O.S. in a t.t. add 4 c.c. conc. $NH_4OH$, cork the tube and shake vigorously with cooling until crystals separate. (The period of shaking required will be ½–1 min. for the methyl ester and 2–3 min. for the ethyl ester.) Filter off the solid, carefully wash it with cold water, dry, and determine the m.p.

179° Benzyl chloride. $C_6H_5{\cdot}CH_2Cl$. Very irritating odour.

β-Naphthyl ether, m.p. 99°.

206° Benzal chloride (Benzylidene chloride). $C_6H_5{\cdot}CHCl_2$. Very irritating odour.

*Hydrolysis to benzaldehyde.*

Into a 100-c.c. wide-mouthed flask pour ½ c.c. of O.S. and 10 c.c. aq. $Na_2CO_3$ and add some porous pot. Fit the flask with a reflux condenser, heat the contents to boiling and continue boiling for 15 min. Remove the flask and cool,—bitter-almond odour of benzaldehyde.

213° Benzotrichloride. $C_6H_5{\cdot}CCl_3$. Very irritating odour.

*Hydrolysis to benzoic acid*, m.p. 121°.

Proceed as indicated under "Benzal chloride." Filter, and acidify the filtrate with conc. HCl. Cool, filter off the solid and wash it with cold water.

Crystallise the acid from water, dry, and determine the m.p.

**Bromo compounds.**

***Liquids.***

B.p.

38° Ethyl bromide. $CH_3{\cdot}CH_2Br$.

β-Naphthyl ether, m.p. 37°. (Picrate of this ether, m.p. 104°.)

B.p.

60° *iso*-Propyl bromide. $(CH_3)_2CH{\cdot}Br$.
Picrate of β-naphthyl ether, m.p. 92°.

71° *n*-Propyl bromide. $CH_3{\cdot}CH_2{\cdot}CH_2Br$.
β-Naphthyl ether, m.p. 39°. (Picrate of this ether, m.p. 75°.)

131° Ethylene dibromide. $CH_2Br{\cdot}CH_2{\cdot}Br$.
Glycol diphenyl ether, m.p. 97°.

144° Methyl bromoacetate. $CH_2Br{\cdot}COO\,Me$. Lachrymatory.
Proceed as indicated under "Ethyl bromoacetate" (below).

151° Bromoform. $CHBr_3$.
Apply the tests under "Chloroform" (page 140), when similar results will be obtained.

159° Ethyl bromoacetate. $CH_2Br{\cdot}COO\,Et$. Lachrymatory.
(*a*) Identify the alkyl radical in the manner described under "Esters of carboxylic acids" (page 100) using half-quantities for the hydrolysis. (Hydrolysis will be complete in 10 min.)
(*b*) Identify the acid constituent by preparing phenoxyacetic acid, m.p. 96°, in the manner described under "Chloroacetic acid" (*b*), page 134. (Use 2 c.c. of O.S., 2 g. phenol, 2 g. KOH and boil for 10 min.)

198° Benzyl bromide. $C_6H_5{\cdot}CH_2Br$. Lachrymatory.
β-Naphthyl ether, m.p. 99°.

***Solids.***

M.p.

92° Carbon tetrabromide. $CBr_4$.
Apply the tests under "Carbon tetrachloride" (page 140), when similar results will be obtained.

**Iodo compounds.**

***Liquids.***

B.p.

43° Methyl iodide. $CH_3{\cdot}I$.
β-Naphthyl ether, m.p. 72°. (Picrate of this ether, m.p. 118°.)

72° Ethyl iodide. $CH_3{\cdot}CH_2I$.
β-Naphthyl ether, m.p. 37°. (Picrate of this ether, m.p. 104°.)

89° *iso*-Propyl iodide. $(CH_3)_2CH{\cdot}I$.
Picrate of β-naphthyl ether, m.p. 92°.

102° *n*-Propyl iodide. $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}I$.
β-Naphthyl ether, m.p. 39°. (Picrate of this ether, m.p. 75°.)

**Solids.**

| M.p. | | |
|---|---|---|
| 119° | Iodoform. $CHI_3$. | Yellow. Characteristic odour. Apply the tests under "Chloroform" (page 140), when similar results will be obtained. |

### METHODS OF PREPARATION OF THE ETHERS INDICATED UNDER THE HALOGEN COMPOUNDS IN THE FOREGOING LISTS

(See sections on "Crystallisation" and "Drying of substances," pages 16–21.)

**β-Naphthyl ethers.**

In a 100-c.c. wide-mouthed flask place 2 g. β-naphthol, 1 g. KOH, 1 c.c. of O.S., 10 c.c. of alcohol and some porous pot. Fit the flask with a reflux condenser, heat the contents to boiling and continue boiling for a suitable period of time (10 min. for ethyl, *n*-propyl, and *iso*-propyl bromides; 5 min. for methyl, ethyl, *n*-propyl, and *iso*-propyl iodides, also for benzyl chloride and bromide).

Add 20 c.c. water and 1–2 g. solid KOH, cool and shake until solid separates (see note below). Filter off the solid, wash it with cold water, crystallise it from alcohol, dry, and determine the m.p.

NOTE.

If the b.p. indicates that O.S. is an ethyl, *n*-propyl, or *iso*-propyl halide, proceed as follows:—Add another 20 c.c. water, connect the flask to a water condenser and distil, changing the receiver when solid appears in the distillate. Continue distilling, adding, if necessary, boiling water to the contents of the flask, until no more solid passes over. Allow the water to run out of the condenser, so that the solid, which has collected in the inner tube, will melt and run into the receiver. Filter the distillate, wash the solid with cold water, dry, and determine the m.p.

If, instead of a solid, an oil distils over (as will usually occur if O.S. is an *iso*-propyl halide), extract it from the distillate with ether (see page 21). Distil off the ether and to the residual liquid add a cold soln. of ⅛-in. layer of picric acid in a t.t. in 3 c.c. alcohol. Stir, filter off the solid picrate, carefully wash it with alcohol, dry, and determine the m.p.

**Preparation of picrates of β-naphthyl ethers (see note).**

To ⅛-in. layer of the ether in a t.t. add 1 c.c. alcohol and heat until solution is complete. Next dissolve ⅛-in. layer of picric acid in a t.t. in 3 c.c. hot alcohol. Cool the solutions, then mix and shake. (The picrate of β-naphthyl ethyl ether separates quickly, that of β-naphthyl *n*-propyl ether only after standing for some time.) Filter off the picrate, carefully wash it with alcohol, dry, and determine the m.p.

NOTE.

Owing to the slight solubility of β-naphthyl methyl ether in cold alcohol, the following method should be employed :—

Heat 0·2 g. of the ether with just sufficient alcohol to effect complete solution. Next dissolve 0·3 g. of picric acid in just sufficient hot alcohol to prevent it from separating out on cooling. Heat both solutions just to boiling and mix them. Cool, filter off the solid picrate, recrystallise it from alcohol, dry, and determine the m.p.

**Phenyl ethers.**

Proceed as under "β-Naphthyl ethers," using 1 c.c. of O.S., 10 c.c. alcohol and the quantities of phenol and KOH given below under the name of the ether to be prepared. Boil for the time stated and observe any special instructions for crystallising.

*Glycerol diphenyl ether* from

(*a*) epichlorhydrin—2½ g. phenol, 1½ g. KOH.
(*b*) glycerol α- or β-dichlorhydrin—2½ g. phenol, 2 g. KOH. (Both dichlorhydrins are first converted by the KOH to epichlorhydrin.)

Boil for 5 min. ; add 40 c.c. water. To crystallise, heat with just sufficient alcohol to effect solution, cool and add water, drop by drop, until pptn. just commences. Stir, filter, etc.

*Glycol diphenyl ether* from ethylene dibromide.
—2 g. phenol, 1½ g. KOH. Boil for ½ hr.

## *ADDITIONAL ALIPHATIC HALOGEN-HYDROCARBONS, ETC.*

For further properties and derivatives a more comprehensive work should be consulted. The halogen may be estimated by the method described on page 151.

**Chloro compounds.**

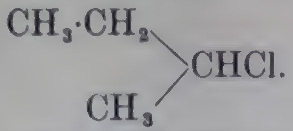
***Liquids.***

*Float on water.*

| B.p. | |
|---|---|
| 37° | *iso*-Propyl chloride. $(CH_3)_2CH{\cdot}Cl$. |
| 46° | *n*-Propyl chloride. $CH_3{\cdot}CH_2{\cdot}CH_2Cl$. Pleasant odour. |
| 46° | Allyl chloride. $CH_2 : CH{\cdot}CH_2Cl$. Mustard-like odour. 1 c.c. decolourises ½ c.c. of a soln. of Br in $CCl_4$ within 1 min. |
| 52° | *tert*-Butyl chloride. $(CH_3)_3CCl$. |

B.p.

67° *sec*-Butyl chloride.



$\begin{matrix} CH_3\cdot CH_2 \\ CH_3 \end{matrix}\!\!>CHCl.$

68° *iso*-Butyl chloride. $(CH_3)_2CH\cdot CH_2Cl$.

77° *n*-Butyl chloride. $CH_3\cdot[CH_2]_3Cl$.

100° *iso*-Amyl chloride. $(CH_3)_2CH\cdot CH_2\cdot CH_2Cl$.

106° *n*-Amyl chloride. $CH_3\cdot[CH_2]_4Cl$.

*Sink in water.*

41° Methylene dichloride. $CH_2Cl_2$.

55° *sym*-Dichloroethylene. $CHCl : CHCl$.

Unsaturated, but 1 c.c. will not decolourise ½ c.c. of a soln. of Br in $CCl_4$ in 15 min.

58° Ethylidene chloride. $CH_3\cdot CHCl_2$.

84° Ethylene dichloride. (*sym*-Dichloroethane.) $CH_2Cl\cdot CH_2Cl$.

88° Trichloroethylene. $CHCl : CCl_2$.

Unsaturated, but 1 c.c. will not decolourise ½ c.c. of a soln. of Br in $CCl_4$ in 15 min.

98° Propylene dichloride. $CH_3\cdot CHCl\cdot CH_2Cl$.

120° Trimethylene dichloride. $CH_2Cl\cdot CH_2\cdot CH_2Cl$.

121° Tetrachloroethylene (Perchloroethylene). $CCl_2 : CCl_2$.

Unsaturated, but 1 c.c. will not decolourise ½ c.c. of a soln. of Br in $CCl_4$ in 15 min.

147° *sym*-Tetrachloroethane. (Acetylene tetrachloride.) $CHCl_2\cdot CHCl_2$.

158° Glycerol trichlorohydrin. $CH_2Cl\cdot CHCl\cdot CH_2Cl$.

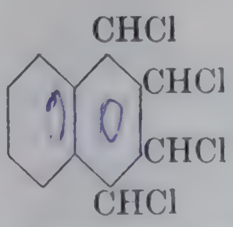
159° Pentachloroethane. $CHCl_2\cdot CCl_3$.

178° ββ′-Dichloroethyl ether. $(CH_2Cl\cdot CH_2)_2O$.

*Solids.*

M.p.

184° Naphthalene tetrachloride.



185° Hexachloroethane. $CCl_3\cdot CCl_3$. Camphor-like odour. (Sublimes)

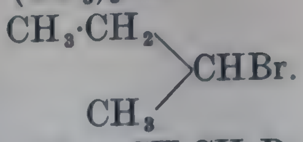
**Bromo compounds.**

***Liquids.*** (*Sink in water.*)

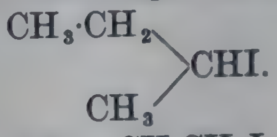
B.p.

70° Allyl bromide. $CH_2 : CH\cdot CH_2Br$. Mustard-like odour.

Unsaturated, but 1 c.c. requires 20–30 min. for the decolourisation of ½ c.c. of a soln. of Br in $CCl_4$.

| B.p. | | |
|---|---|---|
| 72° | *tert*-Butyl bromide. | $(CH_3)_3CBr$. |
| 90° | *sec*-Butyl bromide. |  $CH_3\cdot CH_2(CH_3)CHBr$. |
| 92° | *iso*-Butyl bromide. | $(CH_3)_2\cdot CH\cdot CH_2Br$. |
| 97° | Methylene dibromide. | $CH_2Br_2$. |
| 100° | *n*-Butyl bromide. | $CH_3\cdot[CH_2]_3Br$. |
| 120° | *iso*-Amyl bromide. | $(CH_3)_2CH\cdot CH_2\cdot CH_2Br$. |
| 128° | *n*-Amyl bromide. | $CH_3[CH_2]_4Br$. |
| 142° | Propylene dibromide. | $CH_3\cdot CHBr\cdot CH_2Br$. |
| 165° | Trimethylene dibromide. | $CH_2Br\cdot CH_2\cdot CH_2Br$. |
| 200° decomp. | *sym*-Tetrabromoethane (Acetylene tetrabromide). | $CHBr_2\cdot CHBr_2$. |
| 219° | Glycerol tribromohydrin. | $CH_2Br\cdot CHBr\cdot CH_2Br$. |

**Iodo compounds.** (*Sink in water.*)

| B.p. | | |
|---|---|---|
| 100° | *tert*-Butyl iodide. | $(CH_3)_3CI$. |
| 101° | Allyl iodide. | $CH_2 : CH\cdot CH_2I$. Leek-like odour. |
| 118° | *sec*-Butyl iodide. |  $CH_3\cdot CH_2(CH_3)CHI$. |
| 120° | *iso*-Butyl iodide. | $(CH_3)_2CH\cdot CH_2I$. |
| 130° | *n*-Butyl iodide. | $CH_3\cdot[CH_2]_3I$. |
| 147° | *iso*-Amyl iodide. | $(CH_3)_2CH\cdot CH_2\cdot CH_2I$. |
| 154° | *n*-Amyl iodide. | $CH_3\cdot[CH_2]_4I$. |
| 181° | Methylene di-iodide. | $CH_2I_2$. |

## *AROMATIC HALOGEN-HYDROCARBONS*

*Procedure for the identification of O.S.* :—

Determine the b.p. if liquid, or the m.p. if solid, and refer to the list of b.p.s or m.p.s in the appropriate subsection, according to whether O.S. contains Cl, Br, or I. If one of these b.p.s or m.p.s is identical with, or near to, that of O.S., confirm the identity of O.S. by preparing and determining the m.p. of the derivative there indicated. The methods of preparation of derivatives are given on page 149.

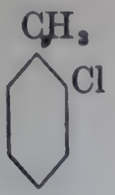
**Chloro-hydrocarbons.**

***Liquid.***

| B.p. | | |
|---|---|---|
| 132° | Chlorobenzene. | $C_6H_5Cl$. |
| | | *p*-Nitro derivative, m.p. 83°. |

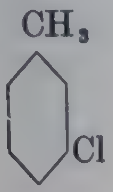
B.p.

159° *o*-Chlorotoluene.



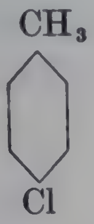
Oxidation→*o*-chlorobenzoic acid, m.p. 140°.

162° *m*-Chlorotoluene.



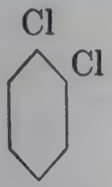
Oxidation→*m*-chlorobenzoic acid, m.p. 153°.

162° *p*-Chlorotoluene.



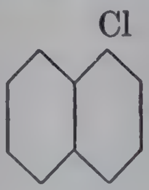
Oxidation→*p*-chlorobenzoic acid, m.p. 236°.

179° *o*-Dichlorobenzene.



Solid derivatives difficult to prepare.

263° α-Chloronaphthalene.

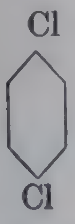


Picrate, m.p. 137°.

*Solid.*

M.p.

53° *p*-Dichlorobenzene.



2 : 5-Dichloronitrobenzene, m.p. 54°. In order to prove that a different substance has been obtained carry out a mixed m.p. determination (see page 14), or apply Test 8B (page 171) when a positive test for a nitro group will be obtained.

**Bromo-hydrocarbons.**

***Liquid.***

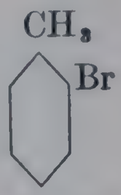
B.p.

155° Bromobenzene. $C_6H_5Br$.

*p*-Nitro derivative, m.p. 126°. (No heating is required in the nitration process described on page 149. Allow the mixture to stand for 5 min., shaking periodically.)

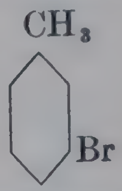
*p*-Bromo derivative, m.p. 89°.

181° *o*-Bromotoluene.



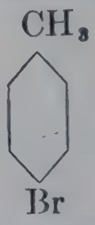
Oxidation→*o*-bromobenzoic acid, m.p. 147°.

183° *m*-Bromotoluene.



Oxidation→*m*-bromobenzoic acid, m.p. 155°.

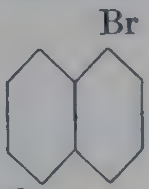
185° *p*-Bromotoluene.



M.p. 28°.

Oxidation→*p*-bromobenzoic acid, m.p. 251°.

280° α-Bromonaphthalene.

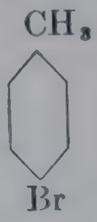


Picrate, m.p. 134°.

***Solid.***

M.p.

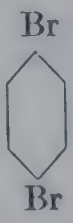
28° *p*-Bromotoluene.



B.p. 185°.

Oxidation→*p*-bromobenzoic acid, m.p. 251°.

89° *p*-Dibromobenzene.



2 : 5-Dibromonitrobenzene, m.p. 84°.

**Iodo-hydrocarbons.**

***Liquid.***

B.p.

188° Iodobenzene. $C_6H_5I$.

*p*-Nitro derivative, m.p. 171°. (No heating is required in the nitration process described on page 149. Allow the mixture to stand for 5 min. Crystallise from acetone and wash the crystals with alcohol.)

*p*-Bromo derivative, m.p. 91°.

## METHODS OF PREPARATION OF THE DERIVATIVES INDICATED UNDER THE HALOGEN-HYDROCARBONS IN THE FOREGOING LISTS

(See sections on "Crystallisation" and "Drying of substances," pages 16–21.)

**Nitro-compounds.**

To 1 c.c. or 1 g. of O.S. in a dry t.t. add a mixture of 1½ c.c. each of conc. $HNO_3$ and conc. $H_2SO_4$. Stand the t.t. in gently boiling water for 5 min., shaking periodically. Cool, add 10 c.c. water and shake. Filter, wash the solid with cold water, crystallise it from alcohol, dry, and determine the m.p.

***p*-Dibromobenzene and *p*-bromoiodobenzene.**

In a 100-c.c. flask place 1 c.c. of O.S., an amount of iodine about equal in bulk to a half-pea and 1 c.c. bromine. Allow to stand for 10 min., then stand the flask in boiling water for a further 10 min. Add 20 c.c. boiling aq. NaOH and shake until the liquids become colourless. Cool and shake, then filter. Wash the solid with cold water, crystallise it from alcohol, dry, and determine the m.p.

**Picrates of α-chloro and α-bromonaphthalene.**

To ⅛-in. layer of picric acid in a t.t. add 3 c.c. alcohol and warm until solution is complete. Cool, add ½ c.c. of O.S. and shake. Filter, crystallise the solid from alcohol, dry, and determine the m.p.

**Oxidation of chloro and bromotoluenes to chloro and bromobenzoic acids.**

In a 100-c.c. wide-mouthed flask place 1 c.c. of O.S., 2½ g. solid $KMnO_4$, 40 c.c. water, 5 drops of aq. NaOH and some porous pot. Fit the flask with a reflux condenser, heat the contents to boiling and continue boiling fairly rapidly for 3 hr. Cool, and pass $SO_2$ until any purple colour and brown ppt. have disappeared. Filter off the white ppt. of halogen acid, wash it with cold water and crystallise from water (or from alcohol if the acid is only sparingly soluble in boiling water). Dry the crystals and determine the m.p.

# ACID HALIDES AND ALKYL CHLOROFORMATES (CHLOROCARBONATES)

*Procedure for the identification of O.S. :—*

Determine the b.p. and refer to the following list of b.p.s. If one of these b.p.s is identical with, or near to, that of O.S., confirm the identity of O.S. by following the given procedure.

B.p.

55° Acetyl chloride. $CH_3{\cdot}COCl$. Pungent odour.

(*a*) To 5 c.c. water in a t.t. add 5 drops of O.S. Pour the soln. into a dish, add dil. $NH_4OH$ until just alkaline, then boil until a piece of red litmus paper momentarily immersed in the soln. is just no longer turned blue, keeping the volume at 4–5 c.c. by the addition, when necessary, of water. Pour 2 c.c. of the soln. into a t.t., cool, and add an equal volume of aq. $FeCl_3$,

—wine-red colour (viewed through the depth of the liquid) due to the formation of $NH_4$ acetate.

(*b*) *Preparation of β-naphthyl acetate*, m.p. 70°.

In a small beaker place 1 g. β-naphthol and 5 c.c. aq. NaOH. Add gradually 1 c.c. of O.S., then add 10 c.c. water, cool and stir. Filter, wash the solid with cold water, crystallise it from a mixture of 2 parts alcohol and 1 part water, dry, and determine the m.p.

71° Methyl chloroformate. Cl·COOMe. Lachrymatory.

Proceed as indicated under "Ethyl chloroformate."

80° Propionyl chloride. $CH_3{\cdot}CH_2{\cdot}COCl$. Pungent odour.

(*a*) Proceed as indicated under "Acetyl chloride" (*a*) when a similar result will be obtained. Also apply Test (*c*), page 68, to confirm the presence of a propionate in the soln.

(*b*) Prepare propionanilide, m.p. 105°, in the manner described under "Acetic anhydride" (page 69).

94° Ethyl chloroformate. Cl·COOEt. Lachrymatory.

Identify the alkyl radical in the manner described under "Details of method of hydrolysis" (page 100) using half-quantities. Hydrolysis will be complete in 5 min.

103° Chloroacetyl chloride. $CH_2Cl{\cdot}COCl$. Pungent odour.

(*a*) Proceed as indicated under "Chloroacetic acid" (page 134), when similar results will be obtained.

B.p. (*b*) *Preparation of chloroacetamide*, m.p. 119°.

To 2 c.c. conc. $NH_4OH$ add 1 c.c. of O.S.; cool and filter. Crystallise the solid from a small quantity of water, dry, and determine the m.p.

197° Benzoyl chloride. $C_6H_5{\cdot}COCl$. Lachrymatory.

(*a*) *Hydrolysis to benzoic acid*, m.p. 121°.

Into a 100-c.c. wide-mouthed flask pour 1 c.c. of O.S. and 10 c.c. aq. NaOH. Fit the flask with a reflux condenser, heat the contents to boiling and continue boiling for 5 min. Cool, acidify with conc. HCl; cool and filter. Wash the solid with cold water, crystallise it from water, dry, and determine the m.p.

(*b*) Prepare benzanilide, m.p. 163°, in the manner described under "Benzoyl derivatives" (*a*), page 217, using 1 c.c. of aniline.

## ESTIMATION OF HALOGEN

### Method of Stepanow, modified by Bacon.

Weigh out 0·2–0·25 g. ($=w$) of the halogen compound and introduce it into a flask of 300–400 c.c. capacity. Add a suitable volume of 98% alcohol ($w \times 156$ c.c. if Cl is present, $w \times 68$ c.c. if Br, and $w \times 44$ c.c. if iodine is present). Fit the flask with a reflux water condenser, heat the contents to boiling, and add gradually through the condenser tube, in pieces about the size of a pea, a suitable quantity of clean sodium ($w \times 19{\cdot}5$ g. if Cl is present, $w \times 8{\cdot}5$ g. if Br, and $w \times 5{\cdot}5$ g. if I is present. The addition should extend over at least 30 min.). When all the sodium has been added boil the mixture for 1 hr. Allow to cool somewhat, then add through the condenser tube a volume of distilled water twice that of the alcohol taken. Remove the alcohol by distilling over about ⅓ of the volume of liquid. Cool the residue in the flask, acidify with dil. $HNO_3$, and add a known volume of $\frac{N}{10}$ $AgNO_3$ solution. Filter off the silver halide, wash the ppt. with distilled water, and allow the washings to run into the first filtrate.

Titrate the excess of $AgNO_3$ in the filtrate with $\frac{N}{10}$ ammonium thiocyanate, using iron alum solution as an indicator (Volhard's method). From the volume of $\frac{N}{10}$ $AgNO_3$ used up calculate the percentage of halogen in the organic compound.

Alternatively, the ppt. of Ag halide may be dried and weighed.

**Additional halogen-aldehydes and halogen-ketones.**

*Liquids.*

B.p.
208° *o*-Chlorobenzaldehyde. $Cl{\cdot}C_6H_4{\cdot}CHO$.
  2 : 4-Dinitrophenylhydrazone, m.p. 207°.
  Oxidation → *o*-chlorobenzoic acid, m.p. 140°.
213° *m*-Chlorobenzaldehyde. $Cl{\cdot}C_6H_4{\cdot}CHO$.
  2 : 4-Dinitrophenylhydrazone, m.p. 245°.
  Oxidation → *m*-chlorobenzoic acid, m.p. 153°.
232° *p*-Chloroacetophenone. $Cl{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3$.
  2 : 4-Dinitrophenylhydrazone, m.p. 239°.
  Oxidation → *p*-chlorobenzoic acid, m.p. 236°.

*Solids.*

M.p.
47° *p*-Chlorobenzaldehyde. $Cl{\cdot}C_6H_4{\cdot}CHO$.
  2 : 4-Dinitrophenylhydrazone, m.p. 265°.
  Oxidation → *p*-chlorobenzoic acid, m.p. 236°.
50° ω-Bromacetophenone (Phenacyl bromide).
  $C_6H_5{\cdot}CO{\cdot}CH_2Br$. Very irritating adour.
  *Preparation of phenacyl benzoate, m.p. 118°.*

In a 100 c.c. wide-mouthed flask place ½ g. of O.S. ½ g. of sodium benzoate, 2½ c.c. of water, and 5 c.c. of alcohol. Boil under a reflux condenser for ½ hr. Cool, filter off the solid, wash it with cold water, crystallise from alcohol, dry, and determine the m.p.

  Oxidation → benzoic acid, m.p. 121°.
51° *p*-Bromacetophenone. $Br{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3$.
  2 : 4-Dinitrophenylhydrazone, m.p. 235°.
  Oxidation → *p*-bromobenzoic acid, m.p. 251°.
59° ω-Chloracetophenone (Phenacyl chloride).
  $C_6H_5{\cdot}CO{\cdot}CH_2Cl$. Very irritating odour.
  Phenacyl benzoate, m.p. 118° (see under "ω-Bromacetophenone").
  Oxidation → benzoic acid, m.p. 121°.

*Derivatives.*

2 : 4-Dinitrophenylhydrazones. See page 66.
Oxidation of chlorobenzaldehydes. Proceed as under "Anisaldehyde" (page 62).
Oxidation of halogen-acetophenones. Proceed as under "Oxidation of chloro and bromotoluenes" (page 149).

# SCHEME III

## Compounds containing Sulphur (or Sulphur and Chlorine)

If sulphur only is present proceed as indicated below; if, in addition, chlorine is present, see instead "Sulphochlorides" (page 163).

*O.S. liquid.*

Proceed as indicated under "Esters of sulphuric acid, etc." (page 160).

*O.S. solid.*

If (*a*) no metal is present, follow the procedure under **A.**
(*b*) a metal is present, proceed as indicated under **B.**

### A. No metal present.

To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 5 c.c. water, close the mouth of the tube with the thumb and shake for 15 sec. If any O.S. has remained undissolved, filter. Test the soln. or filtrate with blue litmus paper; if strongly acid proceed as under (1), otherwise as under (2).

(1) To 2 c.c. of the aq. soln. of O.S. add one drop aq. $FeCl_3$. If a violet or red colour is obtained see "Sulphonic acids of phenolic compounds" (page 157), otherwise see "Sulphonic acids of hydrocarbons" (page 158).

(2) Apply the general test for sulphones given on page 163. If the disagreeable garlic-like odour of ethyl mercaptan is obtained identify the sulphone by a m.p. determination; if no such odour is produced proceed as indicated under "Esters of sulphuric acid and sulphonic acids" (page 160).

### B. Metal present.

(1) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. dil. $H_2SO_4$ (1 c.c. conc. $H_2SO_4$ added to 3 c.c. water. See Note, page 154) and heat to boiling. Note if there is a pungent odour of $SO_2$ or not.

If (*a*) $SO_2$ is evolved see "Bisulphite compounds of aldehydes and ketones, and sulphoxylates" (page 154).
(*b*) no $SO_2$ is evolved apply Test 2.

NOTE.

The strength of acid stated above is employed in order to cause the ready evolution of $SO_2$ from sulphoxylates, a pale yellow ppt. of colloidal sulphur being formed at the same time. Little $SO_2$ is evolved when 2N acid is employed, whereas bisulphite compounds are readily decomposed by this strength of acid.

(2) To $\frac{1}{8}$-in. layer of powdered O.S. in a t.t. add 3 c.c. cold distilled water and shake vigorously for 1 min. Add 3 c.c. conc. HCl and 1 c.c. aq. $BaCl_2$. (If there is any solid present, filter.) Stand the t.t. in boiling water for 5 min. If a white ppt. ($BaSO_4$) is formed, see "Salts of alkyl sulphuric acids" (page 156), otherwise apply Test 3.

(3) Dissolve R.G. of O.S. in 2 c.c. distilled water. To the cold soln. add one drop aq. $FeCl_3$.

If a violet or red colour is obtained see "Sulphonic acids of phenolic compounds and their salts" (page 157), otherwise see "Sulphonic acids of hydrocarbons and their salts" (page 158).

## *BISULPHITE COMPOUNDS OF ALDEHYDES AND KETONES, AND SULPHOXYLATES*

NOTE.

Ketones in which the carbonyl group is directly attached to a benzene ring (e.g. acetophenone, benzophenone) and mesityl oxide do not form bisulphite compounds.

*Procedure for the identification of O.S.* by liberation and recognitio of the aldehyde or ketone :—

To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. aq. $Na_2CO_3$ and hea to boiling. Note the odour and appearance of the mixture ; cool If there is obtained

(*a*) a clear, colourless soln. proceed as under **A**.

(*b*) a yellow colour, white emulsion, or oily drops (which ma solidify on cooling), proceed as under **B** (page 156).

NOTE.

The liberated aldehyde or ketone may often be recognised b its odour ; its identity, however, should be confirmed in th manner described under **A** or **B**.

**A.** In a 100-c.c. wide-mouthed flask place 1 g. of O.S., 20 c.c of aq. $Na_2CO_3$ and some porous pot. Connect the flask to water condenser, and use a t.t. as the receiver. Distil unt 5–6 c.c. is present in the receiver. Proceed according to whethe or not a liquid is seen to be floating on the surface of the a distillate.

**No liquid on the surface of the distillate.**

To 1 c.c. of the distillate add an equal volume of Schiff's reagent, shake, and allow to stand for *2 min.* Do not heat the mixture. If a deep violet or red colour is obtained proceed as under (*a*); if, however, no colour, or only a faint colour is obtained, proceed as under (*b*).

(*a*) To 2 c.c. of the distillate add an equal volume of 20% aq. KOH, heat to boiling and continue boiling for ¼ min.

If the soln.

(i) becomes yellow, and a yellow ppt., changing to orange, with a disagreeable odour is obtained, this indicates that acetaldehyde is present in the distillate. Confirm as follows :—

To 2 c.c. of the distillate add an equal volume of ½% aq. sodium nitroprusside, then add 5 drops aq. NaOH, —deep wine-red colour.

(ii) remains clear and colourless, apply the following test for formaldehyde :—

To 2 c.c. of the distillate add R.G. of resorcinol, then pour 2 c.c. conc. $H_2SO_4$ (from another t.t.) carefully down the side of the tube. A red ring at the junction of the liquids, and the formation of a white ppt. (which changes to violet-red) in the aq. soln., indicates that O.S. is the bisulphite compound of formaldehyde, or, if a ppt. of colloidal sulphur was obtained on heating O.S. with $H_2SO_4$, sodium formaldehyde sulphoxylate,

$$CH_2(OH){\cdot}SO_2Na.$$

(*b*) Add one drop of the distillate to 2 c.c. of iodine soln., then add aq. NaOH, drop by drop, until the deep brown colour disappears. An immediate, pale yellow ppt. of iodoform, with characteristic odour, indicates that O.S. may be the bisulphite compound of acetone or methyl ethyl ketone. To distinguish between the two ketones add to 2 c.c. of the distillate an equal volume of ½% aq. sodium nitroprusside, then add 2 drops aq. NaOH. When a deep wine-red colour has developed, acidify with acetic acid. With acetone the colour changes to a violet-red, whereas with methyl ethyl ketone there is little or no change in colour. For further distinction distil another gram of O.S. with aq. $Na_2CO_3$, and prepare a 2 : 4-dinitrophenylhydrazone, using the whole of the distillate. (For method of preparation see page 65).

2 : 4-dinitrophenylhydrazone of acetone, m.p. 126°
" " " methyl ethyl ketone, m.p. 111°.

**Liquid floating on the surface of the distillate.**

From the distillate prepare a 2 : 4-dinitrophenylhydrazone (see page 66) and determine its m.p.

M.p.
122° suggests that the liquid is *n*-butyraldehyde.
143° ,, ,, ,, ,, ,, methyl *n*-propyl ketone.
155° ,, ,, ,, ,, ,, propionaldehyde.
160° ,, ,, ,, ,, ,, *cyclo*hexanone.

B. Warm 2 g. of O.S. with 20 c.c. aq. $Na_2CO_3$ ; cool. Separate the liberated aldehyde or ketone if solid by filtration, or if liquid by extraction with ether (see page 21). Identify the aldehyde or ketone by preparing and determining the m.p. of a suitable derivative (see pages 65–66). Below are the results obtained by heating the bisulphite compounds of a few common aromatic aldehydes with aq. $Na_2CO_3$.

Yellow colour, odour of cinnamon, with bisulphite compound of cinnamaldehyde (page 62)

Clear, yellow soln., aromatic odour with bisulphite compound of salicylaldehyde (page 64)

White emulsion with oily drops
- bitter-almond odour with bisulphite compound of benzaldehyde (page 61)
- characteristic odour with bisulphite compound
  - of anisaldehyde (page 62)
  - of phenylacetaldehyde (page 62)

White emulsion, or oily drops yielding a solid on cooling — faint, fragrant odour, with bisulphite compound of piperonal (page 63.)

## *SALTS OF ALKYLSULPHURIC ACIDS*

**Identification of the alkyl radical.**

Into a 100-c.c. wide-mouthed flask pour 10 c.c. water, add 3 c.c. conc. $H_2SO_4$ and cool. Add 2 g. of O.S. and some porous pot and boil under a reflux condenser for 5 min. ; *cool.* Connect the flask to a sloping condenser and add to the contents 5 c.c. dichromate mixture. Distil, using a t.t. as the receiver, until 5–6 c.c. of distillate is obtained. Test the distillate in the manner described under " No liquid on the surface of the distillate " (page 155). A positive test for acetaldehyde indicates that O.S. is a salt of ethylsulphuric acid, $Et{\cdot}SO_4H$, and a positive test for formaldehyde indicates that O.S. is a salt of methylsulphuric acid, $CH_3{\cdot}SO_4H$, and so on.

## *SULPHONIC ACIDS OF PHENOLIC COMPOUNDS AND THEIR SALTS*

Only sulphosalicylic acid and its salts, and the salts of *p*-phenolsulphonic acid (sulphocarbolates) are here considered. These yield a violet or violet-red colour on the addition of aq. $FeCl_3$ to their aqueous solutions.

*Procedure:—*

To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. dil. $HNO_3$ (1 c.c. conc. $HNO_3$ diluted to 10 c.c. with water). Stand the t.t. in water at 70° for *2 min.*

If there is obtained

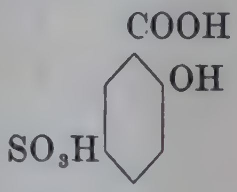
(*a*) a colourless, or faint yellow soln. with or without a ppt., see "Sulphosalicylic acid and its salts."

(*b*) a red-brown soln. with or without a ppt., see "Salts of *p*-phenolsulphonic acid" (page 157).

NOTE:

A ppt. will be due to the formation of a sparingly soluble sulphate, e.g. $BaSO_4$.

### Sulphosalicylic acid (Salicylsulphonic acid) and its salts.

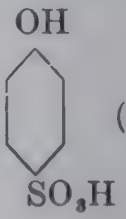


(M.p. of anhydrous acid 120°. Hygroscopic.)

Confirm the identity of O.S. by hydrolysis to salicylic acid, m.p. 158°, as follows:—

Into a 100-c.c. beaker pour 5 c.c. water and add 5 c.c. conc. $H_2SO_4$, an amount of O.S. equivalent to $\frac{1}{2}$-in. layer in a t.t. and some porous pot. Invert over the beaker a $3\frac{1}{2}$-in. glass funnel. Heat the contents of the beaker to boiling and continue boiling gently for 5 min. A sublimate of salicylic acid will collect on the funnel. Place the funnel in the neck of a separating funnel and wash the deposited crystals into the latter with ether. Wash the ethereal soln. three times with about 3 c.c. water in order to remove $H_2SO_4$. Distil off the ether (see page 21), dry the residue and determine its m.p.

### Salts of *p*-phenolsulphonic acid (phenolsulphonates, or sulphocarbolates).



Apply the following confirmatory tests for *p*-phenolsulphonates.

(*a*) To $\frac{1}{8}$-in. layer of O.S. in a dry t.t. add 1 c.c. conc. $HNO_3$. Stand the t.t. for 5 min. in a 400-c.c. beaker containing about 200 c.c. of water which has been heated to boiling and from which the flame has been removed. (If a metal such as Na, K, or Zn, is present, a clear soln. will be obtained; if, however, a metal such as Ca or Ba is present, a ppt. of sulphate will be formed.) Remove the t.t. and nearly fill it with water,—intense yellow colour, due to the formation of picric acid. Apply the following test for picric acid:—(If a ppt. was formed on heating the salt with $HNO_3$, filter.) To 2 c.c. of the yellow soln. add aq. NaOH until the soln. is alkaline (the colour will change to orange). Add 2 drops $NH_4$ sulphide and stand the t.t. in boiling water for 1 min.,—deep red colour (due to an alkali salt of picramic acid, formed by the partial reduction of picric acid).

(*b*) *Preparation of tribromophenol*, m.p. 93°.

In a boiling-tube place the equivalent of $\frac{1}{2}$-in. layer of O.S. in a t.t. and add 20 c.c. water. Heat to boiling and add strong Br soln. (10 c.c. Br, 15 g. KBr, 100 c.c. water) until the colour of the Br persists after shaking. Cool, filter, and wash the solid with cold water. Transfer the solid to a t.t., add 5 c.c. aq. NaOH and shake. Dilute with an equal volume of water and filter.

Acidify the filtrate with conc. HCl, filter off the ppt., wash it well with cold water, dry, and determine the m.p.

(*c*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. dichromate mixture and heat to boiling,
—pungent odour of *p*-benzoquinone, indicating that O.S. is a para compound.

## *SULPHONIC ACIDS OF HYDROCARBONS AND THEIR SALTS*

*Procedure for the identification of O.S.*:—

Prepare and determine the m.p. of the corresponding sulphonamide (see page 159), then refer to the list of m.p.s of sulphonamides (page 159). In order to distinguish between two sulphonic acids or salts, the m.p.s of whose sulphonamides are identical, or close together, prepare and determine the m.p. of the ester there indicated (see page 160).

**Note.**

A confirmatory test for naphthalene-1-sulphonic acid is the production of naphthalene on carrying out the process of desulphonation described on page 160.

| *Sulphon-amide* M.p. | *Sulphonic acid* (*or salt*) *indicated* | *Phenyl ester* M.p. | *β-Naphthyl ester* M.p. | *Sulpho-chloride* |
|---|---|---|---|---|
| 137° | *p*-Toluenesulphonic acid<br>$CH_3{\cdot}C_6H_4{\cdot}SO_3H$ | 95° | | M.p. 69° |
| | *m*-Xylene-4-sulphonic acid<br>$(CH_3)_2C_6H_3{\cdot}SO_3H(1:3:4)$ | 65° | | Oil |
| 150° | Naphthalene-1-sulphonic acid<br>$C_{10}H_7{\cdot}SO_3H$ | 75° | | M.p. 67° |
| 153° | Benzenesulphonic acid<br>$C_6H_5{\cdot}SO_3H$ | 35° | 106° | Oil |
| 154° | *o*-Toluenesulphonic acid<br>$CH_3{\cdot}C_6H_4{\cdot}SO_3H$ | 52° | 97° | Oil |
| 212° | Naphthalene-2-sulphonic acid<br>$C_{10}H_7{\cdot}SO_3H$ | 98° | | M.p. 76° |

**Preparation of derivatives of sulphonic acids.**

(See sections on "Crystallisation", and "Drying of Substances", pages 16–21.)

First prepare the sulphonic chloride as follows :—In a porcelain dish place 2 g. of O.S. and add 4 g. $PCl_5$. Grind the substances intimately together by means of a pestle. If the mixture does not become liquid or semi-solid (which will usually occur if O.S. is a free sulphonic acid or an alkali salt) heat on a water bath for 10 min. Cool, wash the contents of the dish with water into a separating funnel and extract with ether (see page 21).

Divide the ethereal soln. into two equal portions, distil off the ether from each portion in separate flasks and cool the residues. (Chlorides of *p*-toluenesulphonic acid and of the naphthalene sulphonic acids solidify, whereas those of benzenesulphonic acid, *o*-toluenesulphonic acid, and *m*-xylene-4-sulphonic acid remain liquid.) Proceed with these residues as follows :—

(*a*) *Preparation of the sulphonamide.*

Into one of the flasks containing the residue of sulphonic chloride (which should be melted if it has solidified) pour 10 c.c. conc. $NH_4OH$ and stir. (The sulphonamide thus formed is usually yellow ; the colour, however, disappears during subsequent operations.) Add 20 c.c. water and boil down to about $\frac{1}{3}$ of the volume in order to remove excess of ammonia, then just acidify with dil. HCl.

If the sulphonamide

(1) has dissolved completely, evaporate down until crystals separate from a cooled portion. Cool, filter, wash the solid with cold water, and recrystallise it from water.

(2) appears to be insoluble in water, filter, wash the solid with water, and crystallise it from alcohol.

Dry, and determine the m.p.

(*b*) *Preparation of the phenyl (or β-naphthyl) ester.*

Dissolve the residue of sulphonic chloride in 5 c.c. acetone and pour the soln. into a 100-c.c. conical flask. Add 1 g. phenol (or β-naphthol) and 30 c.c. aq. NaOH. Cork the flask, cool, and shake, more or less continuously for 10 min. (see Note). If a solid separates dilute with an equal volume of water and filter. Wash the solid with cold water, crystallise it from alcohol, dry, and determine the m.p.

Note.

If no solid separates, extract with petroleum ether (see page 21). Distil off the ether, cool the residue, add 2 c.c. alcohol and stir. The sulphonic ester will usually solidify, either almost immediately, or after standing for a time.

*Desulphonation of naphthalene-1-sulphonic acid (or salt)* :—

Fit a 100-c.c. wide-mouthed flask with a cork and reflux condenser. Remove the flask and pour into it 5 c.c. water. Add 5 c.c. conc. $H_2SO_4$, some porous pot and the equivalent of $\frac{1}{4}$-in. layer of O.S. in a t.t. Attach the flask to the condenser, heat the contents to boiling and continue boiling gently for 5 min. A white sublimate of naphthalene, with characteristic odour, will appear in the condenser.

## *ESTERS OF SULPHURIC ACID AND OF SULPHONIC ACIDS*

In the following procedure for identification only the esters named in the lists (pages 161–2) are considered.

**Hydrolysis.**

Fit a 100-c.c. flask, having a short wide neck and flat bottom, with a cork and a reflux condenser. Remove the flask from the condenser and place in it 25 c.c. of 20% aq. KOH, some porous pot and 3 c.c. or g. of O.S.

Connect the flask again to the condenser, heat the contents to boiling and continue boiling for 45 min., unless the layer of ester completely disappears in a shorter period of time.

If the layer of ester has completely disappeared proceed as under **A**, otherwise as under **B** (page 161).

**A.** Pour 10 c.c. water through the condenser into the flask. Disconnect the flask and attach it to a sloping condenser. Distil, using a t.t. as the receiver, until 10 c.c. of distillate is obtained. Pour the alkaline residue into a beaker and keep it for the treatment described later.

Rinse out the flask with water, pour in the distillate, add 20 c.c.

dichromate mixture and some porous pot. Connect the flask to the sloping condenser and distil, using a t.t. as the receiver, until about 7 c.c. of distillate is obtained. Test the distillate for the presence of formaldehyde or formic acid, or of acetaldehyde in the manner described under **A** (page 39) in order to ascertain whether O.S. is a methyl or an ethyl ester.

*Treatment of the alkaline residue.*

If O.S. is a liquid, acidify 2 c.c. of the alkaline residue with dil. HCl and add two or three drops of aq. $BaCl_2$. A white ppt. indicates that O.S. is an ester of sulphuric acid. See list of esters of sulphuric acid (page 161).

If no white ppt. is obtained, or if O.S. is a solid, proceed as under **B,** "Treatment of the alkaline residue" (page 161) in order to identify the sulphonic acid.

**B.** Repeat the hydrolysis, but using 5 g. of solid KOH and 25 c.c. of alcohol instead of the 25 c.c. of 20% aq. KOH and boiling gently for 15 min. Add 25 c.c. water and distil off 20–25 c.c. of liquid in order to remove most of the alcohol. Pour the residue in the flask into a 100-c.c. cylinder, make up to 50 c.c. with water and proceed as indicated under "No alcohol has been detected" (page 104) in order to isolate and identify the phenolic constituent of the ester.

*Treatment of the alkaline residue* (after extraction of the phenol with ether).

Acidify with conc. HCl, pour the soln. into a dish and evaporate to dryness on a water bath. Identify the sulphonic acid in the residue by preparing a sulphonamide (see page 159) and determining its m.p. (The m.p. of *p*-toluenesulphonamide is 137°.)

NOTE.

If the whole of the residue be employed, 4 g. of $PCl_5$ should be added. Owing to the presence of KCl the mixture will not usually become liquid or semi-solid, and it is advisable to heat it on a water bath for 10–15 min. in order to complete the reaction.

### Esters of sulphuric acid.

(3 c.c. completely hydrolysed by boiling with 25 c.c. of 20% aq. KOH for 5 min.)

| B.p. | |
|---|---|
| 188° | Methyl sulphate. $(CH_3)_2SO_4$. |

CAUTION.

Great care should be taken when using dimethyl sulphate, since not only is the vapour highly poisonous, but the liquid is absorbed readily through the skin with toxic results. If spilt on the hands wash immediately with conc. $NH_4OH$, in order to hydrolyse the sulphate before it can be absorbed through the skin.

*Preparation of β-naphthyl methyl ether*, m.p. 72°.

In a 100-c.c. flask place 1 g. of β-naphthol and 5 c.c. aq. NaOH. Add 1 c.c. of O.S. and shake until solid separates. (This will usually occur in 1–2 min.). Add 20 c.c. water, shake and filter. Wash the solid with cold water, crystallise it from alcohol, dry, and determine the m.p.

208° Ethyl sulphate. $(C_2H_5)_2SO_4$.

*Preparation of β-naphthyl ethyl ether*, m.p. 37°.

In a 100-c.c. wide-mouthed flask place 1 g. of β-naphthol, 5 c.c. aq. NaOH and 1 c.c. of O.S. Shake for 5 min., then add 10 c.c. of 20% aq. KOH and some porous pot.

Fit the flask with a cork and reflux condenser, heat the contents of the flask to boiling and continue boiling for 5 min. in order to destroy the excess of sulphate. Add 20 c.c. water, connect the flask to a sloping condenser and distil until no oily liquid remains in the flask, adding more water if necessary. Filter off the solid which has collected in the receiver, wash it with cold water, dry and determine the m.p.

**Esters of *p*-toluenesulphonic acid.** $CH_3$ $SO_2{\cdot}OR$.

*Alkyl esters.* (3 g. completely hydrolysed by 25 c.c. of boiling 20% aq. KOH in the time indicated.)

| *M.p.* | | *Time required for hydrolysis.* |
|---|---|---|
| 28° | Methyl *p*-toluenesulphonate | 15 min. |
| 32° | Ethyl ,, | 40 min. |

*Aryl esters.* (3 g. completely hydrolysed by boiling for 15 min. with 5 g. solid KOH and 25 c.c. alcohol.)

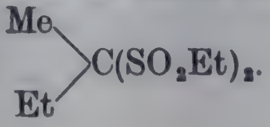
| *M.p.* | |
|---|---|
| 50° | *m*-Cresol *p*-toluenesulphonate |
| 53° | *o*-Cresol ,, |
| 69° | *p*-Cresol ,, |
| 71° | Thymol ,, |
| 85° | Guaiacol ,, |
| 89° | α-Naphthol ,, |
| 95° | Phenol ,, |
| 125° | β-Naphthol ,, |

## *SULPHONES*

*General test.*

Mix a quantity of O.S., which would about one-third fill the bulb of an ignition tube, with an equal bulk of animal charcoal. Introduce the mixture into the tube and heat,

—disagreeable garlic-like odour of ethyl mercaptan.

| M.p. | | |
|---|---|---|
| 76° | Trional. (Methyl sulphonal) |  $\begin{matrix}Me\\Et\end{matrix}\!\!>\!C(SO_2Et)_2.$ |
| 85° | Tetronal. | $(Et)_2C(SO_2Et)_2.$ |
| 126° | Sulphonal. | $(Me)_2C(SO_2Et)_2.$ |

## *SULPHOCHLORIDES*

To 3 c.c. of distilled water in a t.t. add one drop of O.S. if liquid, or R.G. if solid. Heat to boiling and continue boiling gently for 1 min. Cool, filter if not clear, and add an equal volume of dil. $HNO_3$ and 1 c.c. aq. $AgNO_3$; shake,—white curdy ppt. of AgCl. Refer to the list of sulphochlorides (page 159) and identify O.S. by preparation of the derivatives there indicated.

# SCHEME IV

## Compounds containing N, or N and halogen; also solid compounds containing N with sulphate or phosphate.

If O.S. is a solid proceed as indicated under "O.S. solid" (page 166); if a liquid follow the procedure below.

***O.S. liquid.***

To 1 c.c. of O.S. in a t.t. add 5 c.c. water, close the mouth of the tube and invert twice.

If O.S. has

**A.** dissolved completely in the water, test the soln. with red litmus paper.

If the colour of the paper is

(*a*) changed to a definite blue, see "Aliphatic and heterocyclic amines" (page 213).

(*b*) unaffected, or little affected, proceed as indicated under "O.S. liquid" (page 177). If O.S. is found not to be formamide, proceed as indicated in Test 9*B* (page 171), ignoring (*a*) under "Tests with the 4N soln."

**B.** not dissolved completely in the water, to 1 c.c. of O.S. in a t.t. add 5 c.c. dil. HCl.

If (*a*) a ppt. is obtained (indicating that O.S. is an amine, the hydrochloride of which is sparingly soluble), add 10 c.c. water, heat to boiling, and, if the solid has not completely dissolved, continue boiling with shaking for ½ min. Cool, and if any solid is present, filter. With the soln. or filtrate proceed as indicated in Test 4 (page 168), omitting the blank test.

(*b*) no ppt. is obtained, close the mouth of the t.t. and invert twice.

If O.S. has

(i) dissolved completely in the acid, to the soln. apply Test 4 (page 168), omitting the blank test. If in this test neither a red-brown colour nor an emulsion is produced, and no red dye is obtained on adding the "resultant liquid" to alkaline β-naphthol, see "Aliphatic and heterocyclic amines" (page 213).

(ii) not dissolved completely in the acid, apply Test 8*B* (page 171), using 5 drops of O.S.

If in this test no red colour is obtained, apply the tests given under "Alkyl nitrites and nitrates" (page 241); if O.S. is thus found not to be a nitrite or nitrate, proceed as indicated in Test 9*B* (page 171) ignoring (*a*) under "Tests with the 4N soln."

***O.S. solid.***

If O.S. contains

(*a*) a metal, proceed as indicated under "Metal present" (page 173).

(*b*) no metal, follow the procedure below.

**No metal present.**

If O.S. possesses a deep yellow colour (e.g. like that of *p*-nitroaniline), or an orange or red colour see Section 7 (page 220); if colourless, pale yellow, brownish, or violet, apply Test 1.

(1) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. aq. NaOH. If an intense yellow or orange colour (similar to that obtained by the action of aq. NaOH on picric acid) is produced see Section 7 (page 220); if no such colour is obtained, hold a narrow strip of moistened red litmus paper in the mouth of the tube, taking care not to touch the glass. If within 30 sec. of adding the aq. NaOH the colour of the litmus paper is changed to a definite blue, see "Ammonium salts" (page 176) unless O.S. is a halide salt or sulphate in which case see "Salts of aliphatic amines" (page 216). If the litmus paper is unaffected, or little affected, shake the t.t. for 2–3 min.; the gradual development of a deep red or deep brown colour indicates that O.S. is an aminophenol, or a salt of an aminophenol (see page 203). Should no deep red or deep brown colour develop, heat the contents of the t.t. to boiling and continue boiling for $\frac{1}{2}$ min. Test for alkaline vapours in the manner already described. (If no intense yellow, orange, red-brown, or red colour is produced, retain the contents of the t.t. in case they may be required for Test 5.)

If (*a*) an intense yellow, or orange colour is produced, then if the disagreeable odour of aldehyde resin is present ($NH_3$ will also have been evolved) see "Acetaldehyde-ammonia" (page 236), or if this odour is not present, apply Test 8*B* (page 171).

(*b*) a red-brown or red colour is obtained, apply Test 8*B* (page 171).

(*c*) no intense yellow, orange, red-brown, or red colour is obtained, but alkaline vapours are evolved, then to $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. aq. NaOH, and stand the t.t. in gently boiling water for *1 min.* Remove the t.t. from the water, and hold, for a minute or so, a narrow strip of moistened red litmus paper in the mouth of the tube, taking care not to touch the glass.

If the colour of the litmus paper is changed to a definite blue see " Amides and imides " (page 177); if unaffected or little affected, apply Test 3.

NOTE.—In addition to the evolution of $NH_3$ the bitter-almond odour of benzaldehyde would be obtained with hydrobenzamide, $(C_6H_5CH)_3N_2$, m.p. 102°; an odour somewhat similar to that of benzaldehyde, however, is obtained when benzamide (see page 179) is boiled with aq. NaOH.

(*d*) none of the results described under (*a*), (*b*), and (*c*) is obtained, apply Test 2, unless O.S. is a halide salt, sulphate, or phosphate, in which case apply Test 3.

(2) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. dil. $H_2SO_4$, heat to boiling, continue boiling for $\frac{1}{2}$ min. and note the odour of the evolved vapours.

If these smell of

(*a*) formaldehyde (pungent odour), then if the soln. is colourless see " Hexamine " (page 236), or if yellow-brown in colour see " Methyleneaniline " (page 236).

(*b*) benzaldehyde (bitter-almond odour) " see Derivatives of benzaldehyde " (page 237).

(*c*) neither formaldehyde nor benzaldehyde, apply Test 3.

(3) To a measured $\frac{1}{8}$-in. layer of powdered O.S. in a dry $\frac{5}{8}$-in. t.t. add *5 c.c.* distilled water and heat to boiling; if O.S. has not dissolved completely, continue boiling with shaking for $\frac{1}{2}$ min. (If any oil or solid is present, filter.) Test the hot soln. or filtrate with blue litmus paper; note if definitely acid or not. (Use will be made of this knowledge later.) Cool and shake well) note any separation of solid. (If a solid dissolves completely in the boiling water and does not separate out at all on cooling and shaking, it will be described for the purpose of the scheme as " readily soluble in water," otherwise as " sparingly soluble in water."

***O.S. readily soluble in water.***

If the aq. soln. is

(i) definitely acid, apply Test 4.

(ii) not acid, test it with red litmus paper. If the colour of the paper is changed to a definite blue see " Amines " (page 208); if the litmus paper is unaffected, or little affected, apply Test 4 to the aq. soln.

***O.S. sparingly soluble in water.***

To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 5 c.c. dil. HCl, heat to boiling and continue boiling with shaking for $\frac{1}{2}$ min.; cool. (If the contents of the t.t. have set to a solid mass, add 10 c.c. water, boil again, and cool.) If any solid is present, filter. To this soln. or filtrate apply Test 4.

NOTE.

If the solid dissolves completely in the boiling dil. HCl, it will be described for the purpose of the scheme as "readily soluble in dil. HCl," otherwise as "not readily soluble in dil. HCl."

(4) Prepare a soln. of nitrous acid as follows:—To 3 c.c. of $2\frac{1}{2}\%$ aq. $NaNO_2$ add an equal volume of dil. HCl; mix by closing the mouth of the t.t. and inverting; do not shake. (An approximately $2\frac{1}{2}\%$ aq. soln. of $NaNO_2$ may be prepared by dissolving $\frac{1}{4}$-in. layer of the solid in a t.t. in 20 c.c. water.) To 3 c.c. of the cold aqueous or acid soln. of O.S. and also to 3 c.c. dil. HCl (as a blank test) add, without shaking, an equal volume of the prepared nitrous acid soln.

If with the O.S. soln. this produces

(*a*) a colourless soln., with very much greater evolution of gas than that from the blank see Section 2, **A** (page 184); if the evolution of gas is only slightly greater, first proceed as indicated under (*d*).

(*b*) an immediate red-brown, green, or violet-blue coloured ppt. or soln. see Section 5 (page 210).

(*c*) a white or yellow emulsion, proceed as indicated in Section 4 (page 206).

(*d*) a result different from those described under (*a*), (*b*) and (*c*) add 2 c.c. of the resultant liquid to alkaline β-naphthol. ($\frac{1}{8}$-in. layer of β-naphthol in a t.t. dissolved in 5 c.c. aq. NaOH.) An immediate, intense orange-red, red, or brown-violet coloured ppt. or soln. (due to the formation of an azo colour) indicates $—NH_2$ directly attached to an aromatic nucleus. See Section 3 (page 187).

If any other result (yellow colour, etc.) is obtained, proceed as follows:—

If O.S. is a sulphate or phosphate, apply Test 7; if it is not one of these salts, then if it is

(i) readily soluble in water or in dil. HCl, repeat Test 4 and stand both t.t.s in boiling water for 15 sec., then remove. If the evolution of gas from the O.S.

soln. is very much greater than that from the blank see "Aliphatic amino-acids" (page 185); if not appreciably different from that of the blank, apply Test 5 unless O.S. contains halogen, in which case apply Test 7.

(ii) not readily soluble in dil. HCl, apply the test under "Carbazole" (page 208); if a negative result is obtained, apply Test 5 unless O.S. contains halogen, in which case apply Test 8.

(5) If no solid is present in the contents of the t.t. reserved in Test 1 just *acidify* with conc. HCl, then cool and shake; if any solid is present dilute with an equal volume of water and filter before acidifying.

If (*a*) no ppt. is produced, apply Test 6.

(*b*) a ppt. is obtained, add R.G. of O.S. to 2 c.c. aq. $Na_2CO_3$, heat to boiling, then cool. Add 1 c.c. aq. $AgNO_3$ and shake.

A dark grey or black ppt. indicates that O.S. is uric acid; confirm by applying Test 6.

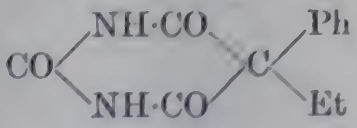
If no dark grey or black ppt. is obtained, add R.G. of O.S. to 5 c.c. water and heat to boiling. Cool, and if any solid is present, filter. Divide the soln. or filtrate into two approximately equal parts; reserve one of these in case it is required for the test given under (ii).

To the other part of the soln. add one drop of Denigès soln.

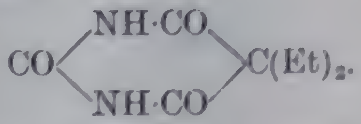
If (i) a white ppt. is obtained, determine the m.p. of O.S.

M.p.

173°-177° indicates that O.S. is phenobarbitone (luminal),



189°-192° indicates that O.S. is barbitone (veronal),



(ii) no ppt. is produced, proceed as directed in Test 6, and, if necessary, as in Test 7; then if this does not lead to the identification of

O.S. add one drop of aq. $FeCl_3$ to the reserved portion of the soln. If a violet colour is obtained see "Derivatives of phenolic acids" (page 183); otherwise apply Test 8.

(6) Pour 5 c.c. of a saturated aq. soln. of Br into a porcelain dish, stir in R.G. of O.S., then evaporate to dryness on a water bath.

If there is obtained an orange residue, becoming reddish on cooling, *and violet-red on holding over conc. $NH_4OH$* (Murexide test), proceed as indicated under "Purine group" (page 242). If any other result is obtained apply Test 7.

(7) To 2 c.c. dil. HCl add R.G. of O.S., heat to boiling with shaking, then cool. Add 2 drops of Mayer's reagent.

If (*a*) a white or pale yellow ppt. is obtained see "Alkaloids" (page 244).

(*b*) no ppt. is obtained, apply Test 8 unless O.S. is a halide salt or sulphate, in which case see "Salts of aliphatic and heterocyclic amines" (page 216).

(8) *A*. Into a 100-c.c. flask pour 5 c.c. conc. HCl and 5 c.c. water. Heat the contents of the flask to boiling, and add the equivalent of $\frac{1}{8}$-in. layer in a t.t. of O.S. Continue gently boiling, shaking round frequently, for 5 min. Add 20 c.c. water, shake round and cool; if any oil or solid is present, filter. To 2 c.c. of the cold soln. or filtrate add 2 c.c. of $2\frac{1}{2}\%$ aq. $NaNO_2$ (ignore any emulsion or slight ppt. formed). Pour the mixture into alkaline β-naphthol ($\frac{1}{8}$-in. layer of β-naphthol in a t.t. dissolved in 5 c.c. aq. NaOH). If an immediate, intense, orange-red or red coloured ppt. or soln. is

(*a*) obtained, proceed as indicated under "Acetyl derivatives of aromatic primary monamines" (page 200). If acetic acid is detected in the distillate, determine the m.p. of O.S. and refer to the lists of m.p.s of acetyl derivatives (pages 187, 217). If the m.p. of O.S. is near to that of two or more acetyl derivatives, follow the procedure under (*b*), page 201.

Should no acetic acid be detected in the distillate, apply Test 9*B*.

(*b*) not obtained, to 3 c.c. of the acid soln. or filtrate add aq. NaOH until the mixture is just alkaline. Heat to boiling and add 1 c.c. Fehling's soln. (equal volumes of No. 1 and No. 2).

If (i) immediate reduction occurs (i.e. blue colour disappears and an orange or red ppt. is formed) see "Oximes and semicarbazones" (page 237).

(ii) no reduction occurs, proceed as indicated under *B*.

*B*. Repeat Test *A* with the addition of 1 g. solid $SnCl_2$ to the mixture. The immediate formation of an intense, orange-red or red coloured ppt. or soln. with the alkaline $\beta$-naphthol indicates that O.S. has been reduced by the $SnCl_2$ and HCl to an aromatic primary amino compound ($NH_2$ in nucleus).

See Section 7 (page 220).

If no orange-red or red coloured ppt. or soln. is obtained, apply Test 9 unless the aq. soln. of O.S. was found in Test 3 to be strongly acid, in which case see "Acyl aliphatic amino-acids" (page 186).

(9) *A*. In a dry t.t. place R.G. of O.S., one drop of $2\frac{1}{2}\%$ aq. $NaNO_2$ and 2 c.c. conc. $H_2SO_4$; warm gently and shake.

If a deep blue colour is obtained see "Derivatives of diphenylamine" (page 208); if no blue colour is produced proceed as indicated under *B*.

*B*. In a 100-c.c. wide-mouthed flask place $\frac{1}{2}$ g. of O.S., 15 c.c. of a mixture of equal volumes of water and conc. $H_2SO_4$ and some porous pot. Fit the flask with a reflux condenser, heat the contents to boiling and continue boiling for 15 min., periodically loosening the condenser clamp and giving the flask a rotary movement. If O.S. has not dissolved completely, boil for a further 15 min.

Detach the flask from the condenser. (Acetic acid, or phenylacetic acid, if present, may be detected by their odour.)

If in the condenser tube there is

(i) a white sublimate, wash it with about 10 c.c. ether into a small separating funnel. Wash the ethereal soln. three times with about 3 c.c. water in order to remove $H_2SO_4$. Distil off the ether (see page 21), dry the residue, determine the m.p. and refer to the list of m.p.s of sparingly soluble acids (page 75).

(ii) no sublimate, allow the contents of the flask to cool somewhat, then add gradually 20 c.c. of boiling water. Connect the flask to a condenser, and distil until 10 c.c. of distillate is obtained.

If only a liquid distillate is obtained, test it for the presence of acetic acid or propionic acid in the manner described on page 68.

Should solid be present in the condenser tube, wash it with water into the receiver; filter, wash the solid with cold water, dry, determine the m.p. and refer to the lists of sparingly soluble acids (pages 75–79).

*Treatment of the residue in the flask.*

To the contents of the flask add 40 c.c. boiling water and shake round. Cool, and make up the volume with water to 70 c.c. (The $H_2SO_4$ will now be approximately 4N.)

If the soln. is not perfectly clear, filter until this condition is attained. (If much solid is present in the filter, and no acid has been detected in (i) and (ii), pour 5 c.c. of boiling aq. $Na_2CO_3$ through the filter; reheat the filtrate and pour again through the filter. Cool the filtrate, and just acidify with conc. HCl. If a ppt. is obtained, filter, wash the solid with cold water, dry, determine the m.p. and refer to the lists of m.p.s of sparingly soluble acids (pages 75–79).

*Tests with the 4N soln.*

(*a*) To 10 c.c. of the 4N soln. add 1 c.c. of $2\frac{1}{2}\%$ aq. $NaNO_2$, mix by closing the mouth of the t.t. and inverting. Allow to stand for 2 min.

If a white or pale yellow emulsion is produced, proceed as indicated under "Nitrosamine test" (below); if no emulsion is obtained, add 1 c.c. of the mixture to alkaline β-naphthol. ($\frac{1}{8}$-in. layer of β-naphthol in a t.t. dissolved in 5 c.c. aq. NaOH.) If an immediate, intense, orange-red or red coloured ppt. or soln. is obtained, then if benzoic acid has been detected see "Benzoyl derivatives of aromatic primary monamines" (page 201); or if any acid other than benzoic, or no acid has been detected, see "Anilides" (page 202).

(*b*) To 3 c.c. of the 4N soln. add solid NaOH until the mixture is alkaline. Test for $NH_3$ by smell, and by holding a strip of moistened red litmus paper in the mouth of the tube, taking care not to touch the glass. If $NH_3$ is evolved, see "Nitriles" (page 240).

*Nitrosamine test.*

Pour 25 c.c. of the 4N soln., obtained in Test 9*B* after hydrolysis, into a separating funnel, add 1 c.c. of $2\frac{1}{2}\%$ aq. $NaNO_2$, shake round, and allow to stand for 5 min. Add the equivalent of $\frac{1}{4}$-in. layer in a t.t. of urea (to destroy excess of nitrous acid), leave the funnel unstoppered, shake round, and allow to stand for 5 min. Add 10 c.c. ether (see page 21), insert the stopper, shake, and allow to stand until two well-defined layers are formed. Run off the lower layer, and wash the upper ethereal layer with successive quantities of water (3 c.c.) until the lower aqueous layer, after running off, gives no blue colour on the addition of starch iodide soln. Separate as much water as possible from the ethereal soln. Pour 1 c.c. of the latter through the neck of the funnel into a dry t.t., and evaporate off the ether by immersing the end of the t.t. in hot water. Dry the residue by revolving the end of the t.t. over a small flame. Cool, add R.G. of phenol and 5 drops conc. $H_2SO_4$, and rotate the t.t. in order to mix the contents. A blue-green or blue colour, turned violet-red by a drop of water, and blue on adding aq. NaOH until the mixture is alkaline, indicates a nitrosamine (Liebermann's reaction), formed by the action of nitrous acid on the sulphate of a secondary amine, produced by the hydrolysis of O.S. with the $H_2SO_4$.

If acetic acid has been detected in the distillate (Test 9*B*, page 171) see "Acetyl derivatives of aromatic secondary amines" (page 217); or if benzoic acid has been detected, see "Benzoyl derivatives of aromatic secondary amines" (page 218).

**Metal present.**

(Only compounds containing an alkali metal are here considered.)

*Procedure* :—

To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. water, heat just to boiling, then cool. If the colour of the soln. is yellow, orange, or red, proceed as indicated under **A**, otherwise as indicated under **B** (page 174).

**A.** If (*a*) a yellow or orange-coloured soln. was obtained, add 2 drops of it to 5 c.c. water. To half of this diluted soln. add one drop aq. $FeCl_3$; a deep blue colour indicates that O.S. is a ferrocyanide, e.g. $K_4Fe(CN)_6$. If a deep blue colour is not obtained, to the other half of the diluted soln. add R.G. of powdered $FeSO_4$ and shake; a deep blue colour indicates that O.S. is a ferricyanide, e.g. $K_3\,Fe(CN)_6$. If negative results have been obtained proceed as indicated under "Benzoates" (page 52), but omitting the acetone.

The formation of a solid benzoyl derivative indicates that O.S. is a nitrophenate. (It may be necessary to repeat the procedure, using aq. $Na_2CO_3$ instead of aq. NaOH, as 2 : 4-dinitrophenyl benzoate is readily hydrolised by aq. NaOH.)

*M.p. of benzoate.*

95° indicates that O.S. is a *m*-nitrophenate.
132° „ „ „ „ 2 : 4-dinitrophenate.
142° „ „ „ „ *p*-nitrophenate.

(*b*) a red soln. was obtained, apply the following tests for a nitroprusside (e.g. $Na_2Fe(CN)_5{\cdot}NO$) :—

(i) Add one drop of the red soln. to 2 c.c. water, then add one drop of acetone and 2 drops aq. NaOH, —wine-red colour develops, turned violet-red by acetic acid.

(ii) Add one drop of the red soln. to 10 c.c. water, then add one drop of ammonium sulphide,
—deep violet colour.

If negative results are obtained, proceed as indicated under "*o*-Nitrophenol" (page 221). Similar results to those given indicate that O.S. is an *o*-nitrophenate.

**B.** If O.S. is completely in solution in the 2 c.c. water, proceed as indicated under (*a*); if not completely in solution, proceed as indicated under (*c*).

(*a*) Test the soln. with red litmus paper; if neutral, proceed as indicated under (*d*); if alkaline, apply the following test for a cyanide (alkali cyanides, e.g. KCN, possess the almond-like odour of prussic acid).

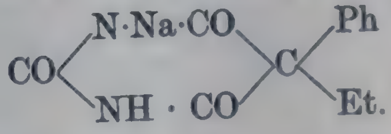
Add one drop of the aq. soln. of O.S. to 5 c.c. water, then add 2 drops aq. NaOH, and R.G. of ferrous sulphate. Heat to boiling, boil for ½ min., cool, and then acidify with conc. HCl,
—deep blue colour.

If O.S. is not a cyanide, apply Test (*b*).

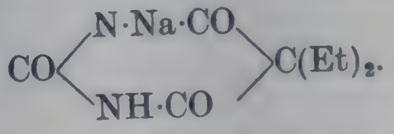
(*b*) To the aq. soln. of O.S. add 1 c.c. dil. HCl and shake. If a white ppt. is obtained, filter it off, wash with cold water, and dry. Add R.G. of the dry ppt. to 5 c.c. water, heat to boiling, cool, and add one drop of Denigé's soln.

If a white ppt. is obtained, determine the m.p. of the dry ppt.

M.p.
173°–177° indicates that O.S. is soluble phenobarbitone,



189°–192° indicates that O.S. is soluble barbitone,



(*c*) To 2 c.c. of aq. $Na_2CO_3$ add R.G. of O.S., heat to boiling, then cool. Add 1 c.c. aq. $AgNO_3$ and shake.

A dark grey or black ppt. indicates that O.S. is a urate. Confirm by applying Test 6 (page 170).

(*d*) To ⅛-in. layer of O.S. in a t.t. add 5 c.c. dil. HCl, heat to boiling, continue boiling for ½ min., then cool. If any solid is present, filter. To the soln. or filtrate add an equal volume of 2½% aq. $NaNO_2$, mix by closing the mouth of the t.t. and inverting. Add 1 c.c. of this soln. to alkaline

$\beta$-naphthol ($\frac{1}{8}$-in. layer of $\beta$-naphthol in a t.t. dissolved in 5 c.c. aq. NaOH).

If a red coloured ppt. or soln. is obtained, prepare about 5 c.c. of a cold, conc. aq. soln. of O.S. and acidify with glacial acetic acid. Filter off the pptd. acid, wash it with cold water, and dry. Proceed as indicated under " Aromatic amino- and acetylamino-acids " (page 199).

If no red coloured ppt. or soln. is obtained with the alkaline $\beta$-naphthol, proceed as indicated under (*e*).

(*e*) Apply Test 8*B* (page 171).

If a red coloured ppt. or soln. is obtained, prepare about 5 c.c. of a cold, conc. aq. soln. of O.S., and acidify with conc. HCl. Filter off the pptd. acid, wash it with cold water, and dry. Proceed as indicated in Section 7 (page 220).

If no red coloured ppt. or soln. is obtained with the alkaline $\beta$-naphthol, proceed as indicated under " Hippuric acid " (page 186); similar results indicate that O.S. is a hippurate. If negative results are obtained, and O.S. contains K, apply Test (*a*) under " Phthalimide, etc." (page 180). A positive result indicates that O.S. is K phthalimide or K succinimide. Apply Test (*c*) page 181); a positive result indicates that O.S. is K phthalimide.

## *SECTION 1*

# *AMMONIUM SALTS: AMIDES AND IMIDES*

## AMMONIUM SALTS OF CARBOXYLIC ACIDS, AND AMMONIUM URATE

*Procedure for the identification of the acid* :—

If O.S. contains halogen proceed as indicated under "Metal present" (page 133), otherwise proceed as follows :—

To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 5 c.c. water and heat to boiling. If O.S. has not dissolved completely, continue boiling with shaking for $\frac{1}{2}$ min. Cool and shake vigorously, filter if any solid is present. (If the solid dissolved completely in the boiling water and has not separated out at all on cooling and shaking, it will be termed "readily soluble," otherwise "sparingly soluble.")

To 2 c.c. of the cold aq. soln. or filtrate add dil. HCl until just acid and shake.

If (1) *a ppt. is obtained*, then if O.S. is readily soluble proceed as under (*a*), or, if O.S. is sparingly soluble, proceed as under (*b*).

(*a*) Acidify the remainder of the aq. soln. with HCl, filter off the pptd. acid and wash it with cold water. Crystallise the acid from water or alcohol, dry, and apply the alkali-zinc test for N.

*If N is absent*, examine the acid as under *B* (page 74).

*If N is present*, apply to the acid (regarded as O.S.) Tests 3 and 4 (page 167), and if necessary Test 8 *B* (page 171) in order to ascertain the nature of the N-containing group present, and refer to the section indicated.

(*b*) To 2 c.c. aq. $Na_2CO_3$ add R.G. of O.S., heat to boiling, then cool. Add 1 c.c. aq. $AgNO_3$ and shake.

A dark grey or black ppt. indicates that O.S. is ammonium urate. Confirm by applying Test 6 (page 170).

(2) *no ppt. is obtained*, test O.S. as indicated under "Salts of carboxylic acids," Procedure I (page 87); if this procedure gives negative results with the $CaCl_2$ and $FeCl_3$ tests, proceed as indicated under "Amides and imides," O.S. solid, *A* (below).

## AMIDES AND IMIDES

### *O.S. liquid.*

Apply the following tests for "Formamide," $H{\cdot}CONH_2$.

(*a*) To 2 c.c. aq. $HgCl_2$ add one drop of O.S., heat to boiling and continue boiling for 10 sec.,—white ppt. of $Hg_2Cl_2$.

(*b*) Heat ⅛-in. layer of O.S. in a t.t.,—strong odour of $NH_3$.

(*c*) To ⅛-in. layer of O.S. in a t.t. add 2 c.c. water, shake to mix, and then add 2 c.c. aq. $FeCl_3$,
—wine-red colour (viewed through the depth of the liquid); brown ppt. on boiling.

### *O.S. solid.*

(1) To ⅛-in. layer of O.S. in a t.t. add 5 c.c. distilled water and heat to boiling with shaking. Cool, and if any solid is present, filter. Test the soln. or filtrate with blue litmus paper; if definitely acid proceed as indicated in Section 2, **A** (page 184); if not acid, apply Test 2.

(2) To ⅛-in. layer of O.S. in a t.t. add 2 c.c. dil. HCl. If a brisk effervescence occurs see "Guanidine carbonate" (page 182); if there is no effervescence proceed as indicated below under **A**.

**A. Amides and imides indicated by the evolution of $NH_3$ on heating with aq. NaOH.**

*If O.S. consists of*

(*a*) deliquescent crystals, follow the procedure under "Propionamide" and "Acetamide" (page 178).

(*b*) a white powder, sparingly soluble in boiling water, apply the tests under "Oxamide" (page 181).

*Otherwise* carry out a m.p. determination.

If O.S. has

(*a*) not melted at 215°, apply the tests under "Phthalamide, phthalimide, and succinamide" (page 180).

(*b*) melted at or below 215°, refer to the following appropriate list, according to whether halogen is absent (page 178) or present (page 182), of m.p.s of amides and imides. If one of these m.p.s is identical with, or near to, that of O.S., confirm the identity of O.S. by following the given procedure.

*Halogen absent.*

M.p.

49° Ethyl carbamate. (Urethane.) $NH_2{\cdot}CO{\cdot}OEt.$

52° Methyl carbamate, $NH_2{\cdot}CO{\cdot}OMe.$

(*a*) Fit a t.t. with a cork and bent delivery tube and arrange the apparatus so that the end of the delivery tube dips into about 3 c.c. baryta water contained in another t.t. Detach the t.t. from the cork and place in it O.S. to the depth of $\frac{1}{8}$-in. then add 3 c.c. each of dil. HCl and $2\frac{1}{2}\%$ aq. $NaNO_2$. Attach the t.t. to the cork, heat until a rapid effervescence occurs, and allow the gas to bubble through the baryta water for 1 min. The baryta water will be turned milky, owing to $CO_2$ having been evolved from O.S. Distinguish between ethyl and methyl carbamates by applying Test (*b*).

(*b*) In a 100-c.c. wide-mouthed flask place 1 g. of O.S., 20 c.c. of 20% aq. KOH and some porous pot. Heat the liquid to boiling under a reflux condenser and continue boiling for 5 min. Allow to cool somewhat, then pour 10 c.c. water through the condenser tube. Distil until 10 c.c. of distillate is obtained. Rinse out the flask, pour in the distillate, add 10 c.c. dichromate mixture and some porous pot. Distil until 6–7 c.c. is present in the receiver. Follow the procedure under A (page 39). A positive test for acetaldehyde indicates that O.S. is ethyl carbamate, and a positive test for formaldehyde or formic acid indicates that O.S. is methyl carbamate.

79° Propionamide, $CH_3{\cdot}CH_2{\cdot}CONH_2.$

82° Acetamide, $CH_3{\cdot}CONH_2.$

Pour 10 c.c. aq. NaOH into a porcelain dish and heat to boiling. Add the equivalent of $\frac{1}{4}$-in. layer in a t.t. of O.S., and continue boiling gently for 5 min. Remove the flame, and add dil. $HNO_3$ with stirring until the soln. is just acid. Add dil. $NH_4OH$ until the soln. is just alkaline, then boil until a piece of red litmus paper momentarily immersed in the soln. is just no longer turned blue, keeping the volume between 5 c.c. and 10 c.c. by the addition, when necessary, of water. Cool, and apply Tests (*a*) and (*c*) under "Acetic acid" and "Propionic acid" (page 68).

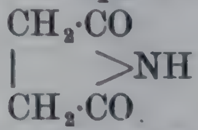
M.p.

114° Ethyl oxamate. (Oxamethane.) $NH_2\cdot CO\cdot COOEt$.

(*a*) Apply Tests (*a*) and (*b*) under "Oxamide" (page 181) when similar results will be obtained.

(*b*) Identify the ethyl radical in the manner indicated under "Esters of carboxylic acids" (page 100), but using 2 g. of O.S. and 10 c.c. dil. $H_2SO_4$ for the hydrolysis. (Considerable frothing occurs when 20% aq. KOH is employed.) Hydrolysis will be complete in 10 min.

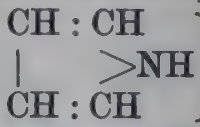
125° Succinimide.



$$\begin{array}{l} CH_2\cdot CO \\ | \qquad > NH \\ CH_2\cdot CO \end{array}$$

(*a*) Mix together 3 R.G. of O.S. and twice this bulk of zinc dust. Introduce the mixture into an ignition tube and heat. Hold a wooden matchstalk, the end of which has been well moistened with conc. HCl, in the evolved vapour.

If the end of the matchstalk is turned a deep red {due to the vapour of pyrrole,



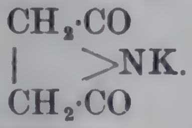
$$\begin{array}{l} CH : CH \\ | \qquad > NH \\ CH : CH \end{array}$$

} succinimide is indicated. Apply Tests (*b*) and (*c*).

If the matchstalk is not coloured red, apply Test (*a*) under "Benzamide."

(*b*) Apply Test (*a*) under "Phthalamide, etc." (page 180), when a similar result will be obtained.

(*c*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 5 c.c. absolute alcohol, heat until solution is complete, then cool. Add an amount of solid KOH about equal in bulk to a pea, cork the tube and shake, —ppt. of K succinimide,



$$\begin{array}{l} CH_2\cdot CO \\ | \qquad > NK. \\ CH_2\cdot CO \end{array}$$

128° Benzamide. $C_6H_5\cdot CONH_2$.

(*a*) Mix 3 R.G. of O.S. with three times this bulk of dry soda-lime. Introduce the mixture into an ignition tube and heat.

A bitter-almond odour of benzonitrile (similar to the odour of nitrobenzene) indicates benzamide. Apply Test (*b*).

If no such odour is obtained, apply Test (*a*) under "Succinimide."

(*b*) *Hydrolysis to benzoic acid*, m.p. 121°.

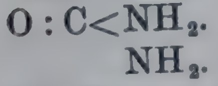
In a 100-c.c. wide-mouthed flask place $\frac{1}{2}$ g. of

M.p.

O.S., 10 c.c. of aq. NaOH and some porous pot. Fit the flask with a reflux condenser, heat the contents to boiling and continue boiling for 10 minutes. Cool, acidify with conc. HCl, cool, and filter.

Wash the solid with cold water, crystallise from water, dry, and determine the m.p.

132° Urea.



$O:C<\begin{matrix}NH_2\\NH_2\end{matrix}$.

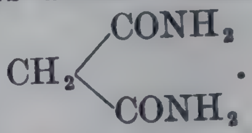
Apply Test 2 (page 184) and also the tests under "Urea" (page 184).

157°. Phenylacetamide. $C_6H_5 \cdot CH_2 \cdot CONH_2$.

*Hydrolysis to phenylacetic acid*, m.p. 76°.

Proceed as under "Benzamide" (*b*) (page 179).

170° Malonamide.

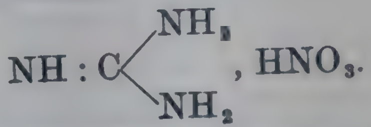


$CH_2<\begin{matrix}CONH_2\\CONH_2\end{matrix}$.

In a t.t. place 3 R.G. of O.S. and add 2 c.c. aq. NaOH and 2 drops aq. $CuSO_4$ (Fehling's No. 1 soln.); shake,

—violet-red colour.

214°. Guanidine nitrate.



$NH:C<\begin{matrix}NH_2\\NH_2\end{matrix}, HNO_3$.

(Aq. soln. neutral since guanidine is a strong base.)

(*a*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. water, heat until solution is complete, then cool. Add (all at once from another t.t.) 2 c.c. of conc. NaOCl soln.,

—vigorous effervescence, *orange colour*.

(*b*) To $\frac{1}{8}$-in. layer of O.S. in a dry t.t. add a few copper turnings and 2 drops conc. $H_2SO_4$; warm,

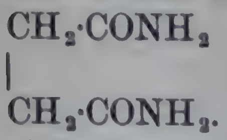
—red fumes of $NO_2$.

Phthalamide, phthalimide, and succinamide.

(*a*) Place R.G. of O.S. in a dry t.t., add 2 drops conc. $H_2SO_4$ and warm. (The amide or imide is thus hydrolysed to the acid.) Add 2 R.G. of resorcinol and gently heat until the mixture is a red brown colour. Cool, add a few drops of water, then add aq. NaOH until the mixture is alkaline. Pour 1 c.c. of the alkaline mixture into a t.t. and fill up with water.

A green fluorescence is obtained with all three compounds. Apply Test (*b*).

(*b*) Proceed as indicated under "Succinimide (*a*)" (page 179). A deep red colour given to the matchstalk indicates that O.S. is succinamide,



$$\begin{array}{l}CH_2\cdot CONH_2\\ |\\ CH_2\cdot CONH_2.\end{array}$$

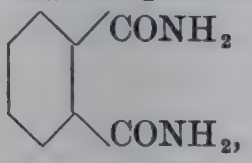
(Decomposes on heating into succinimide and $NH_3$.) If the matchstalk is not coloured red, apply Test (*c*).

(*c*) Proceed as indicated above under (*a*) but using phenol instead of resorcinol. Add the aq. NaOH gradually with shaking until the mixture is alkaline. The red colour of phenolphthalein (destroyed by acid) indicates that O.S. is phthalamide or phthalimide. Distinguish as follows :—

In a boiling tube place the equivalent of $\frac{1}{8}$-in. layer in a t.t. of O.S. and 10 c.c. absolute alcohol. Immerse the end of the tube in water, which has been heated to boiling and allowed to go just off the boil. Shake for 1 min., still keeping the tube in the water.

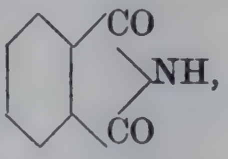
If O.S.

(i) appears practically insoluble phthalamide,



is indicated. (Melts with decomposition, evolving $NH_3$ and leaving a residue of phthalimide.)

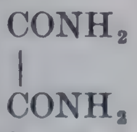
(ii) dissolves more or less completely phthalimide,



is indicated (m.p. 231°).

Confirm as follows :—Cool the alcoholic soln. and pour it into a t.t. Add an amount of solid KOH about equal in bulk to a pea, cork the tube and shake, —ppt. of K phthalimide.

Oxamide. (Sublimes in an open tube.)



$$\begin{array}{l}CONH_2\\ |\\ CONH_2\end{array}$$

(*a*) In a t.t. place 3 R.G. of O.S. and add 5 c.c. aq. NaOH. Heat the liquid to boiling and continue boiling for $\frac{1}{2}$ min. Cool somewhat and acidify with glacial acetic acid.

If the soln. is not perfectly clear, filter until this condition is attained.
Add 2–3 drops aq. $CaCl_2$,
—immediate white ppt. (Ca oxalate.)

(*b*) To $\frac{1}{8}$-in. layer of O.S. in a dry t.t. add 5 drops conc. $H_2SO_4$. Gently warm the mixture by rotating the end of the tube over a small flame, and turn the mouth of the tube periodically to the flame. CO is evolved and burns with a characteristic blue flame.

(*c*) In a t.t. place 3 R.G. of O.S. and add 2 c.c. aq. NaOH and 2 drops aq. $CuSO_4$ (Fehling's No. 1 soln.); shake,
—pink colour.

*Chlorine present.*

M.p.

116° Chloral formamide. (Chloralamide.)
$CCl_3{\cdot}CH(OH){\cdot}NH\ CHO$.

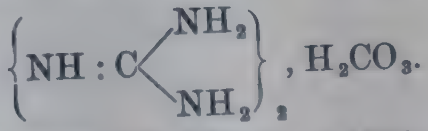
(*a*) To 2 c.c. aq. NaOH add 3 R.G. of resorcinol and R.G. of O.S.; heat to boiling,
—deep red colour, appearing violet-red on shaking.

(*b*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. aq. NaOH, heat to boiling and continue boiling gently for $\frac{1}{2}$ min. Cool, add a drop of phenolphthalein soln., then add dil. HCl until the soln. just becomes colourless. Add 1 c.c. aq. $HgCl_2$, heat to boiling and continue boiling for $\frac{1}{2}$ min.,
—white ppt. ($Hg_2Cl_2$, due to the production of a formate.)

119° Chloroacetamide. $Cl{\cdot}CH_2{\cdot}CONH_2$.
Apply Test (*a*) under "Chloroacetic acid" (page 134), using the equivalent of $\frac{1}{4}$-in. layer in a t.t. of O.S. when a similar result will be obtained.

**B. Amides and imides indicated by special tests.**

Guanidine carbonate,



$$\left\{NH:C\begin{matrix}NH_2\\NH_2\end{matrix}\right\}_2, H_2CO_3.$$

(Indicated by evolution of $CO_2$ on addition of dil. HCl.)
Aq. soln. strongly alkaline.

(*a*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 5 c.c. water, heat until solution is complete, then add 2–3 drops aq. $CaCl_2$,
—white ppt. of $CaCO_3$.

(*b*) Apply Test (*a*) under "Guanidine nitrate" (page 180), when a similar result will be obtained.

(c) *Preparation of guanidine nitrate*, m.p. 214°.

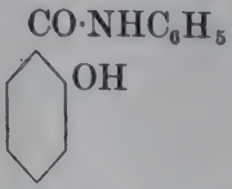
To ¼-in. layer of O.S. in a t.t. add 2 c.c. water, heat until solution is complete, then cool. Add gradually 2 c.c. conc. $HNO_3$; shake and cool. Filter, wash the solid carefully with cold water, dry, and determine the m.p.

***Derivatives of phenolic acids***

(Give a violet-red colour with aq. $FeCl_3$)

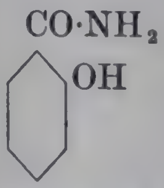
M.p.

135° Salicylanilide.



To R.G. of O.S. in a dry t.t. add 5 drops of conc. $H_2SO_4$. Heat for 10 sec. over a small flame (about 1 in. high), cool and carefully dilute with water to 5 c.c. Again cool, and add 5 c.c. of 2½% aq. $NaNO_2$. Add 2 c.c. of this mixture to alkaline β-naphthol (⅛-in. layer of β-naphthol in a t.t. dissolved in 5 c.c. of approx. 2N. NaOH),—red soln., due to the formation of an azo colour.

138°. Salicylamide,



To ⅛-in. layer of O.S. in a dry t.t. add 5 drops of conc. $H_2SO_4$. Heat for 10 sec. over a small flame (about 1 in. high), cool and carefully dilute with water to 2 c.c. Add sufficient solid NaOH to render the mixture alkaline and hold a strip of moistened red litmus paper in the mouth of the tube, taking care not to touch the glass—paper turned definitely blue, due to evolved $NH_3$.

*Preparation of methyl ether*, m.p. 128°.

In a 100-c.c. flask place 1 g. of O.S., add 5 c.c. aq. NaOH and heat until solution is complete. Add 1 c.c. of dimethylsulphate (see caution, page 161), heat to boiling and continue boiling for 1 min. Cool and shake until solid separates. Filter, wash the solid with cold water, crystallise from aqueous alcohol, dry, and determine the m.p.

## *SECTION 2*

# (*a*) *COMPOUNDS EVOLVING NITROGEN WITH DIL. HCl AND AQ. NaNO₂*

# (*b*) *ACYL ALIPHATIC AMINO-ACIDS*

## A. Compounds evolving nitrogen readily with nitrous acid in the cold.

*Procedure for the identification of O.S.* :—

(1) Heat 2 c.c. Fehling's soln. (equal volumes of No. 1 and No. 2) in a t.t. just to boiling and add R.G. of O.S. If no change occurs apply Test 2. The complete disappearance of the blue colour, and the production of an orange ppt. with some effervescence, indicates that O.S. is a salt of semicarbazide $NH_2{\cdot}NH{\cdot}CO{\cdot}NH_2$. (Aq. soln. will be strongly acid.) Confirm the identity of the base by the preparation of acetone semicarbazone, m.p. 187° (see page 65).

(2) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 3 c.c. of dil. HCl, heat until solution is complete, then cool. Add 3 c.c. of $2\frac{1}{2}\%$ aq. $NaNO_2$, shake, and hold this t.t. for a minute or so over another t.t. containing 3 c.c. of baryta water, as if transferring the contents of the former to the latter, but without allowing any of the liquid to leave the upper t.t. Close the mouth of the lower t.t. with the thumb and shake.

If the baryta water remains clear, see "Salts of aliphatic primary amines" (page 216); if, however, it is turned milky (due to $CO_2$ being evolved from O.S.) proceed as indicated below under "Urea and its salts."

### Urea and its salts

If the aq. soln. of O.S. is neutral, apply the tests given under "Urea"; if strongly acid, proceed as indicated under "Salts of urea" (page 185.)

Urea, $NH_2{\cdot}CO{\cdot}NH_2$, m.p. 132°.

(*a*) *Biuret test.*

Gently heat $\frac{1}{8}$-in. layer of O.S. in a dry t.t. until the melted substance just solidifies. ($NH_3$ will be evolved and a white sublimate formed.) Cool, dissolve the residue (biuret, $NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$) in 1 c.c. warm

aq. NaOH and add one drop aq. $CuSO_4$ (Fehling's No. 1 soln.),
—violet-red colour.

(*b*) *Preparation of urea nitrate*, m.p. 163°.

To ¼-in. layer of O.S. in a t.t. add 2 c.c. water, heat until solution is complete, then cool. Add 2 c.c. conc. $HNO_3$ and cool. Filter, wash the solid carefully with cold water, dry, and determine the m.p.

Salts of urea.

If O.S. is

(i) a chloride, sulphate, or phosphate, prepare urea nitrate in the manner described above under (*b*).

(ii) not a chloride, sulphate, or phosphate, dissolve R.G. of O.S. in 2 c.c. of boiling 50% acetic acid and add 2–3 drops aq. $CaCl_2$.

An immediate white ppt. indicates that O.S. is urea oxalate, m.p. 171°.

If no ppt. is obtained, to ⅛-in. layer of O.S. in a dry t.t. add a few copper turnings and 2 drops conc. $H_2SO_4$; warm.

Red fumes of $NO_2$ indicate that O.S. is urea nitrate, m.p. 163°.

## B. Compounds evolving nitrogen readily with nitrous acid only on heating.

### Aliphatic amino-acids

Refer to the appropriate subsection, i.e. according to whether the aq. soln. of O.S. is neutral or acid.

*Aq. soln. of O.S. neutral.*

Aminoacetic acid (Glycine. Glycocoll), $NH_2 \cdot CH_2 \cdot COOH$, m.p. 232° decomp.

(*a*) To ⅛-in. layer of O.S. in a t.t. add 2 c.c. water, warm until solution is complete, then cool. Add 2 drops of phenolphthalein soln. and 2 drops aq. NaOH, then add an equal volume of neutralised alcohol (alcohol to which phenolphthalein soln. has been added, and then $\frac{N}{10}$ aq. NaOH until just pink),—red colour disappears, indicating the acidic character of O.S.

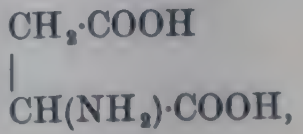
(*b*) Dissolve ⅛-in. layer of O.S. in a t.t. in 2 c.c. water. Add 2 c.c. aq. $CuSO_4$ (Fehling's No. 1 soln.),—blue colour, very much deeper than that of the original aq. $CuSO_4$.

(*c*) *Preparation of benzoyl derivative* (Hippuric acid), m.p. 187°.

In a 100-c.c. flask place 1 g. of O.S., 3 g. $NaHCO_3$ and 20 c.c. water. Shake round, and then add $1\frac{1}{2}$ c.c. benzoyl chloride. Leave the flask uncorked and shake vigorously until the odour of the benzoyl chloride has practically disappeared. Filter, acidify the filtrate with conc. HCl and cool. Filter, wash the solid well with cold water and dry. Transfer the solid to a small beaker, add 10 c.c. of cold benzene and stir well. Filter, and wash the solid with benzene. Crystallise from water, dry, and determine the m.p.

*Aq. soln. of O.S. acid.*

*l*-Aminosuccinic acid (*l*-Aspartic acid),



$$\begin{array}{l} CH_2{\cdot}COOH \\ | \\ CH(NH_2){\cdot}COOH, \end{array}$$

m.p. 270°.

(*a*) Apply Test (*b*) under "Aminoacetic acid," when a similar result will be obtained.

(*b*) Prepare the benzoyl derivative, m.p. 180°, in the manner described under "Aminoacetic acid" (*c*), but using 4 g. of $NaHCO_3$.

### (*b*) Acyl aliphatic amino-acids

Hippuric acid (Benzoyl aminoacetic acid),

$C_6H_5{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}COOH$,

m.p. 187°. Equiv. wt. 179·1.

Apply Test 9*B* (page 171).

If O.S. is hippuric acid a sublimate of benzoic acid (m.p. 121°) will be present in the condenser tube.

To 10 c.c. of the 4N soln. add conc. $NH_4OH$ until alkaline, boil until a piece of red litmus paper momentarily immersed in the soln. is just no longer turned blue, keeping the volume about 5 c.c. by the addition, when necessary, of water. Cool, filter if necessary.

To the soln. and also to an equal volume of water, add aq. $CuSO_4$ (Fehling's No. 1 soln.), drop by drop.

If O.S. is hippuric acid a deeper blue colour will be obtained with the soln. than with the water, due to the presence of amino-acetic acid.

*p*-Nitrobenzyl ester, m.p. 137° (see page 232).

## *SECTION 3*

# *COMPOUNDS YIELDING DIAZONIUM SALTS WITH DIL. HCl AND AQ. $NaNO_2$*

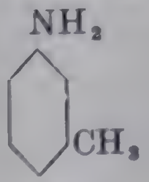
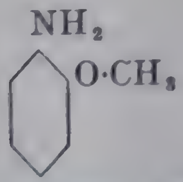
(These compounds will have been indicated by the formation of a red- or brown-violet dye on the addition of their diazonium or tetrazonium salt to alkaline β-naphthol.)

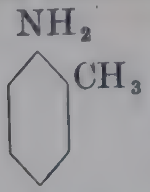
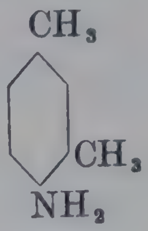
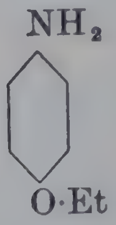
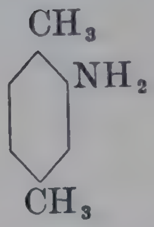
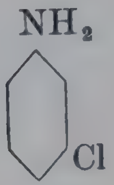
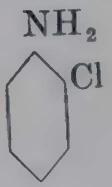
Follow the appropriate procedure, i.e. under "O.S. liquid" (below) or under "O.S. solid" (page 188). The general methods of preparation of derivatives are given on pages 217–8, and the method of determination of equivalent weights on page 218. The equiv. wts. given have been calculated from the formulæ using the following atomic weights :—C = 12·00, H = 1·008, O = 16·00, N = 14·01, Cl = 35·46, Br = 79·92.

### *O.S. liquid.*

Prepare and determine the m.p. of an acetyl derivative, then refer to the appropriate list (according to whether halogen is absent or present) of m.p.s of acetyl derivatives in order to identify the amine. For confirmation of identity, prepare the benzoyl derivative and determine its m.p., or determine the equiv. wt. of O.S.

**Halogen absent**

| *Acetyl derivative M.p.* | *Amine indicated* | | *B.p. of amine* | *Benzoyl deriv. M.p.* | *Equiv. wt. of amine* |
|---|---|---|---|---|---|
| 65° | *m*-Toluidine |  | 199° | 125° | 107·1 |
| 84° | *o*-Anisidine |  | 218° | 64° | 123·1 |
| 101° | Methyl anthranilate. See page 189. | | | | |

| *Acetyl derivative M.p.* | *Amine indicated* | | *B.p. of amine* | *Benzoyl deriv. M.p.* | *Equiv. wt. of amine* |
|---|---|---|---|---|---|
| 110° | *o*-Toluidine |  See note below | 198° | 143° | 107·1 |
| 114° | Aniline | $C_6H_5 \cdot NH_2$ | 184° | 163° | 93·06 |
| 127° | 4-Amino-*m*-xylene |  | 215° | 192° | 121·1 |
| 135° | *p*-Phenetidine |  | 254° | 173° | 137·1 |
| 139° | 2-Amino-*p*-xylene |  | 213° | 140° | 121·1 |
| *Cl present* | | | | | |
| 72° | *m*-Chloroaniline |  | 230° | 120° | 127·5 |
| 87° | *o*-Chloroaniline |  | 207° | 100° | 127·5 |

NOTE.

Aniline may be distinguished from *o*-toluidine as follows :—Just touch the surface of the amine with the extreme tip of a glass rod, and then dip the end of the rod into 5 c.c. water contained in a t.t., and stir for about 10 sec. Add one or two drops of NaOCl soln. (1 c.c. of conc. soln. diluted with water to 10 c.c.). If the amine is aniline a violet colour will be produced. (*o*-Toluidine gives only a yellow-brown colour.)

***O.S. solid.***

If the aq. soln. of O.S. is definitely acid, proceed as indicated under B (page 196) ; if not acid, follow the procedure under A.

### A. Aq. soln. of O.S. not acid.

Determine the m.p. of O.S. and refer to the appropriate list of m.p.s, i.e. according to whether halogen is absent (page 189) or present (page 195). If one of these m.p.s is identical with, or near to, that of O.S. confirm the identity of O.S. by following the given procedure, or by preparing one of the derivatives indicated.

NOTES.

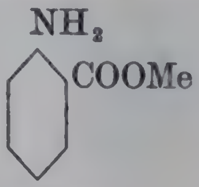
(i) When O.S. has a m.p. identical with, or near to, that of both a free amine and an acetyl derivative of an amine, either the procedure described under "Acetyl derivatives of aromatic primary monamines" (page 200) may be carried out, or an attempt to prepare an acetyl derivative may be made (see page 217). In the former case a positive test for acetic acid in the distillate will indicate that O.S. is an acetyl derivative, while in the latter case, the production of a substance with a m.p. differing widely from that of O.S. will indicate that O.S. is a free amine.

(ii) In the case of a free amine, a determination of the equiv. wt. will provide additional evidence of identity.

**Halogen absent.**

M.p.

25° Methyl anthranilate.



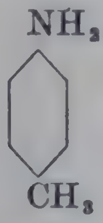
Orange-blossom odour.

Proceed as indicated under "Esters of carboxylic acids" (page 100) but using half-quantities, when a positive test for methyl alcohol will be obtained. (Hydrolysis will be complete in 10 min.)

Acidify the alkaline residue with glacial acetic acid, filter off the pptd. anthranilic acid, wash it with cold water, dry, and confirm its identity by determining its m.p. (144°).

Acetyl derivative, m.p. 101°. Benzoyl derivative, m.p. 100°.

43° *p*-Toluidine.



Powerful characteristic odour.

Acetyl derivative, m.p. 148°. Benzoyl derivative, m.p. 158°. Equiv. wt. 107·1.

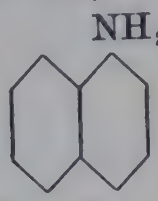
46° Formanilide. $C_6H_5{\cdot}NH{\cdot}CHO$. Faint odour.

(*a*) To $\frac{1}{8}$-in. layer of O.S. in a dry t.t. add 5 drops conc. $H_2SO_4$. Gently warm the mixtures by

M.p. rotating the end of the t.t. over a small flame, and turn the mouth of the tube periodically to the flame. CO is evolved, and burns with a characteristic blue flame.

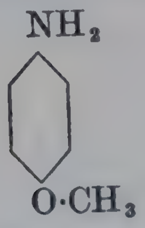
(*b*) In a 100-c.c. wide-mouthed flask place 1 g. of O.S. and 15 c.c. dil. $H_2SO_4$. Boil under a reflux condenser for 5 min., then distil until 5 c.c. of distillate is obtained. To the distillate apply the $HgCl_2$ and $AgNO_3$ tests for formic acid (see page 68, *b*) when positive results will be obtained. From the residual liquid in the flask prepare benzanilide, m.p. 163°, by adding aqueous NaOH until the mixture is alkaline, then adding 2 c.c. benzoyl chloride, etc., as described under "Benzoyl derivatives" (page 217).

50° α-Naphthylamine.



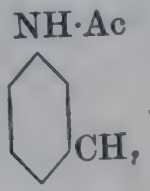
Acetyl derivative, m.p. 159°. Benzoyl derivative, m.p. 160°. Equiv. wt. 143·1.

57° *p*-Anisidine.

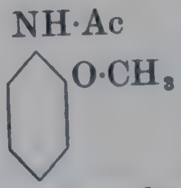


Acetyl derivative, m.p. 127°. Benzoyl derivative, m.p. 154°. Equiv. wt. 123·1.

65° Acetyl *m*-toluidine

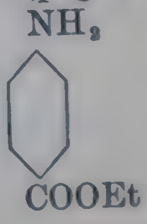


84° Acetyl *o*-anisidine



Proceed as indicated under "Acetyl derivatives of aromatic primary monamines" (page 200).

89° Benzocaine (Ethyl *p*-aminobenzoate).



M.p. Proceed as indicated under "Methyl anthranilate" (m.p. 25°). M.p. of *p*-aminobenzoic acid 186°.

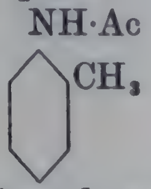
Benzoyl derivative, m.p. 148°.

105° Propionanilide. $C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CH_3$.

Proceed as indicated under "Acetyl derivatives of aromatic primary monamines" (page 200).

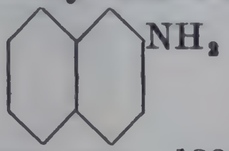
To the distillate apply Test (*c*) (page 68) for propionic acid, when a positive result will be obtained.

110° Acetyl *o*-toluidine.



Proceed as indicated under "Acetyl derivatives of aromatic primary monamines" (page 200).

112° *β*-Naphthylamine.



Acetyl derivative, m.p. 132°. Benzoyl derivative, m.p. 162°. Equiv. wt. 143·1.

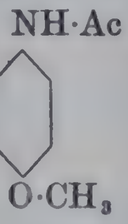
114° Acetanilide. $C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_3$.

(*a*) Proceed as indicated under "Acetyl derivatives of aromatic primary monamines" (page 200).

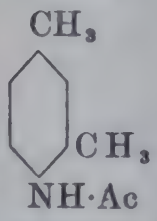
(*b*) *Preparation of* p-*bromoacetanilide*, m.p. 167°.

In a 100-c.c. flask place 1 g. of O.S. and 5 c.c. glacial acetic acid, heat until solution is complete, then cool. Add 4 c.c. of a soln. of 1 c.c. bromine in 9 c.c. glacial acetic acid, and allow to stand for 15 min. Add 50 c.c. water and shake. Filter, wash the solid with water, crystallise from alcohol, dry, and determine the m.p.

127° Acetyl *p*-anisidine



127° Acetyl 4-amino-*m*-xylene

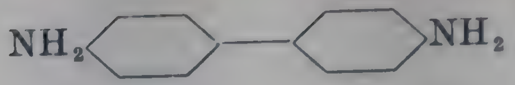


Yield red dyes with alkaline *β*-naphthol in Test 4 (page 168).

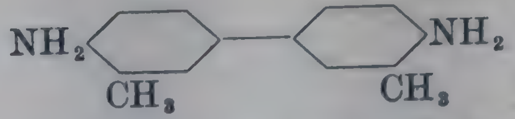
Proceed as indicated under "Acetyl derivatives of aromatic primary monamines" (page 200).

M.p.

127° Benzidine.



129° Tolidine.



Yield brown-violet dyes with alkaline β-naphthol in Test 4 (page 168).

(*a*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. dichromate mixture and heat to boiling,
—pungent odour of *p*-benzoquinone or toluquinone.

(*b*) Dissolve R.G. of O.S. in 2 c.c. warm dil. HCl, cool, add 2 drops dil. $H_2SO_4$ and shake for 1 min. A white ppt. indicates that O.S. is probably benzidine. (Tolidine sulphate is sparingly soluble, but more soluble than benzidine sulphate.)

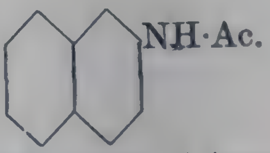
(*c*) To $\frac{1}{4}$-in. layer of O.S. in a t.t. add 5 c.c. alcohol and heat until solution is complete. Cool, filter if not clear. Add 1 c.c. of benzaldehyde and stir. The yellow benzal derivative of benzidine separates immediately, that of tolidine within 1 min.

Filter, wash the solid carefully with acetone, dry, and determine the m.p.

M.p.
232° indicates that O.S. is benzidine.
Equiv. wt. 92·1.
150° indicates that O.S. is tolidine.
Equiv. wt. 106·1.

Acetyl and benzoyl derivatives, owing to their high m.p.s, are not suitable for the identification of these amines.

132° Acetyl β-naphthylamine.



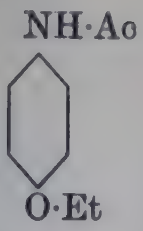
(*a*) Proceed as indicated under "Acetyl derivatives of aromatic primary monamines" (page 200).

(*b*) *Preparation of* 1-*bromo derivative*, m.p. 140°.

In a 100-c.c. beaker place 1 g. of O.S. and 5 c.c. glacial acetic acid, heat until solution is complete, then cool. Add 3 c.c. of a soln. of 1 c.c. bromine in 9 c.c. glacial acetic acid, stir, and allow to stand for 5 min. Filter, wash the solid with glacial acetic acid, crystallise from alcohol, dry, and determine the m.p.

M.p.

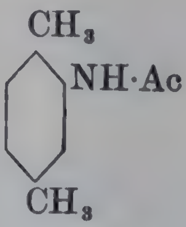
135° Acetyl *p*-phenetidine. (Phenacetin.)



(*a*) Proceed as indicated under " Acetyl derivatives of aromatic primary monamines " (page 200).

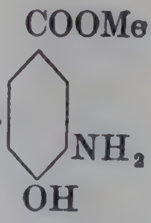
(*b*) *Preparation of 3-nitro derivative* (yellow), m.p. 103°. In a 100-c.c. flask place 1 g. of O.S. and add a mixture of 1 c.c. conc. $HNO_3$ and 9 c.c. water. Stand the flask for 5 min. in boiling water and shake round periodically. Add 20 c.c. water, cool and shake. Filter, wash the solid with water, crystallise from alcohol, dry, and determine the m.p.

139° Acetyl 2-amino-*p*-xylene.



Proceed as indicated under " Acetyl derivatives of aromatic primary monamines " (page 200).

142° Orthocaine (Methyl *m*-amino-*p*-hydroxybenzoate).



(*a*) Dissolve R.G. of O.S. in 5 c.c. water. To the cold soln. add one drop aq. $FeCl_3$,
—violet-red colour, rapidly changing to brown.

(*b*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. aq. NaOH and shake,
—O.S. dissolves readily, owing to the presence of a phenolic group.

Benzoyl derivative, m.p. 242°. (Dissolve 1 g. of O.S. in 5 c.c. cold acetone, add 2 c.c. benzoyl chloride and allow to stand for 5 min. Filter, wash the solid with acetone, dry, and determine the m.p.)

147° Phenylurea. $C_6H_5 \cdot NH \cdot CO \cdot NH_2$.

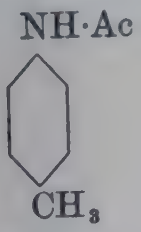
(*a*) Heat $\frac{1}{8}$-in. layer of O.S. in a t.t. above its m.p.,
—strong odour of $NH_3$. (Difference from acetyl *p*-toluidine, m.p. 148°.)

(*b*) *Preparation of diphenylurea (carbanilide)*, $(C_6H_5{\cdot}NH)_2CO$, m.p. 238°.

To $\frac{1}{4}$-in. layer of O.S. in a t.t. add 2 c.c. of freshly distilled aniline. Fit the t.t. with a cork and 2-ft. tube (to serve as an air condenser).

Heat the contents of the t.t. to boiling and continue boiling for 10 min. (The carbanilide separates out as solid. $NH_3$ is evolved and may be detected by holding a strip of moistened red litmus paper in the end of the condenser tube.) Allow to cool, add 10 c.c. boiling dil. HCl, shake and filter. Wash the solid, first with dil. HCl, and then with water. Crystallize from alcohol, dry, and determine the m.p.

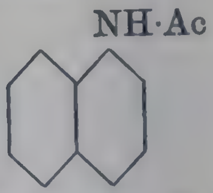
148° Acetyl *p*-toluidine.



Does not yield $NH_3$ on heating above its m.p. (Difference from phenylurea, m.p. 147°.)

Proceed as indicated under "Acetyl derivatives of aromatic primary monamines" (page 200).

159° Acetyl α-naphthylamine.

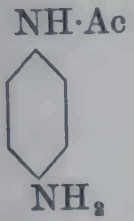


(*a*) Proceed as indicated under "Acetyl derivatives of aromatic primary monamines" (page 200).

(*b*) *Preparation of 4-bromo derivative*, m.p. 193°.

Proceed as indicated under "Acetyl β-naphthylamine" (*b*) page 192, but using 8 c.c. of glacial acetic acid for the solution of O.S.

162° *p*-Aminoacetanilide.



(*a*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 5 c.c. dil. HCl, heat to boiling and continue boiling for $\frac{1}{2}$ min. Dilute with water to 100 c.c.

(i) To 5 c.c. of the diluted soln., add 1 c.c. aq.

$FeCl_3$, then 1 c.c. of a saturated aq. soln. of $H_2S$,
—violet colour.

(ii) To 5 c.c. aq. NaOH add 1 c.c. of the diluted soln. and 1 c.c. of a saturated aq. soln. of phenol, then add 1 c.c. dil. NaOCl soln. (1 c.c. conc. soln. diluted with water to 10 c.c.) Allow to stand for 2 min.,
—deep blue colour.

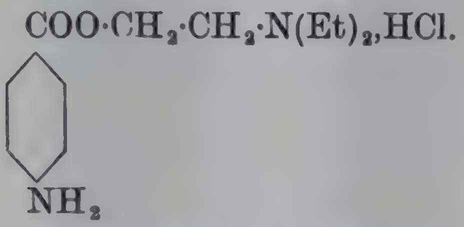
(*b*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. dichromate mixture and heat to boiling,
—pungent odour of *p*-benzoquinone.

(*c*) Proceed as indicated under "Acetyl derivatives of aromatic primary monamines" (page 200), when a positive test for acetic acid in the distillate will be obtained.

**Halogen present.**

AS HALIDE SALT.

M.p.
155° Procaine hydrochloride. (Novocaine. Hydrochloride of diethylaminoethyl-*p*-aminobenzoate.)



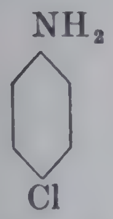
(*a*) Dissolve R.G. of O.S. in 2 c.c. water. To the cold soln. add one drop of Mayer's reagent,
—white ppt., dissolved by adding an equal volume of dil. HCl.

(*b*) Dissolve R.G. of O.S. in 2 c.c. water. To the cold soln. add one drop of iodine soln.,
—red-brown ppt.

NOT AS HALIDE SALT.

*Cl present.*

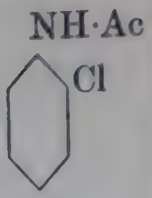
M.p.
70° *p*-Chloroaniline.



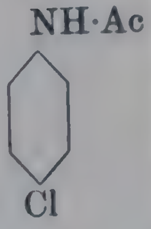
Acetyl derivative, m.p. 178°. Benzoyl derivative, m.p. 192°. Equiv. wt. 127·5.

M.p.

87° Acetyl *o*-chloroaniline



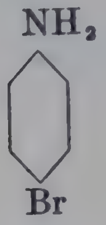
178° Acetyl *p*-chloroaniline



Proceed as indicated under "Acetyl derivatives of aromatic primary monamines" (page 200).

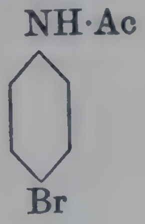
*Br present.*

M.p.
66° *p*-Bromoaniline.



Acetyl derivative, m.p. 167°. Benzoyl derivative m.p. 202°. Equiv. wt. 172·0.

167° Acetyl *p*-bromoaniline.



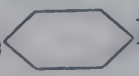
Proceed as indicated under "Acetyl derivatives of aromatic primary monamines" (page 200).

**B. Aq. soln. of O.S. definitely acid.**

*Procedure :—*

To 5 c.c. water add R.G. of O.S. and shake or heat until solution is complete. To the cold soln. add one drop of aq. $FeCl_3$.

If there is obtained

(*a*) a deep green colour, which rapidly changes through red to brown, a salt of *p*-phenylenediamine, $NH_2$  $NH_2$, is indicated. Confirm the identity of the amine by the following tests :—

(i) Dissolve R.G. of O.S. in 10 c.c. water. To the cold soln. add 1 c.c. dil. HCl and then 1 c.c. aq. $FeCl_3$; pass $H_2S$,
—violet-red colour.

(ii) Dissolve R.G. of O.S. in 5 c.c. water. To the cold soln. add 1 c.c. aq. NaOH, 1 c.c. saturated phenol soln. and 1 c.c. dil. NaOCl soln. (1 c.c. conc. soln. diluted with water to 10 c.c.).

—deep blue colour in about one min.

(iii) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. dichromate mixture and heat to boiling,

—pungent odour of *p*-benzoquinone.

(*b*) any result other than that described above under (*a*) follow the procedure given below. (With $FeCl_3$ salts of benzidine and tolidine yield a blue, or persistent green colour, and salts of α-naphthylamine, but not of β-naphthylamine, develop a blue-violet colour.)

*Procedure :—*

To $\frac{1}{4}$-in. layer of O.S. in a t.t. add 2 c.c. aq. NaOH, close the mouth of the t.t., and shake vigorously for 1 min.

If (i) O.S. has dissolved completely, add 1 c.c. glacial acetic acid, *cool well and shake vigorously.*

If a ppt. is obtained see " Aromatic amino- and acetylamino-acids " (page 199).

(ii) an oil or emulsion is produced, see " Salts of aromatic primary monamines " (page 198).

Also see note below.

(iii) a solid is present, then if the diazotised soln. of O.S. gave a red dye with alkaline β-naphthol see " Salts of aromatic primary monamines " (page 198), or if a brown-violet dye was obtained see " Salts of benzidine and tolidine " (page 198).

Also see note below.

NOTE.

If an acid radical has not been already detected add 10 c.c. water to the alkaline mixture, shake and filter. To 2 c.c. of the filtrate in a t.t. add 1 c.c. dil. $H_2SO_4$ and 2 R.G. of powdered $FeSO_4$ ; shake until the latter has dissolved. Pour (from another t.t.) 2 c.c. of conc. $H_2SO_4$ carefully down the side of the tube. A dark brown ring at the junction of the liquids indicates a nitrate.

If a negative result is obtained acidify 2 c.c. of the alkaline filtrate with glacial acetic acid, heat to boiling and add 2–3 drops aq. $CaCl_2$.

A white ppt. indicates an oxalate.

If no ppt. is obtained, acidify the remainder of the alkaline filtrate with dil. $HNO_3$, then add dil. $NH_4OH$ until just alkaline. Pour the soln. into a dish and boil until a piece of red litmus paper momentarily immersed in the soln. is just no longer turned blue, keeping the volume between 5 c.c. and 10 c.c. by the addition, when necessary, of water. Cool, and apply Test (*b*) under **A** (page 87), in order to ascertain if O.S. is an acetate, tartrate, etc.

## Salts of aromatic primary monamines.

*Procedure for the identification of the amine.*

Pour 10 c.c. dil. HCl into a 100-c.c. beaker and heat to boiling. (Many salts of amines are much more soluble in dil. HCl than in water.) Add 2 g. of O.S., continue gently boiling and stir, if necessary adding boiling water, until solution is complete. Allow to cool somewhat, then add 20% KOH until alkaline, cool and stir. If the liberated amine is a solid, filter it off, wash it with cold water and dry; if a liquid, extract with 10 c.c. ether (see page 21) and distil off the solvent. (See note below.) Prepare an acetyl derivative of the amine (see page 217).

If O.S. contains halogen, recrystallise the acetyl derivative and test it for the absence or presence of halogen. Determine the m.p. and refer to the appropriate list (according to whether halogen is absent or present) of m.p.s of acetyl derivatives of liquid or solid aromatic primary monamines (pages 187, 217).

NOTE.

Since the m.p.s of the acetyl derivatives of aniline and *o*-toluidine are close together, the test described under "Note" (page 188) should be carried out with the free amine before preparing the acetyl derivative.

*Salts of benzidine and tolidine.*

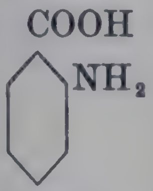
Into a 250-c.c. beaker pour 100 c.c. water and 10 c.c. of 20% aq. KOH, heat to boiling, and add 2 g. of O.S. Continue boiling gently and stir for 5 min., then filter the hot soln. Cool the filtrate, filter off the solid amine, wash it with cold water, and dry. See "Benzidine" and "Tolidine" (page 192.)

### Aromatic amino- and acetylamino- acids

Determine the m.p. of O.S. and follow the procedure under the compound whose m.p. is identical with, or near to, that of O.S.

M.p.

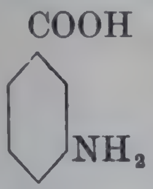
144° *o*-Aminobenzoic acid (Anthranilic acid).



*Preparation of acetyl derivative*, m.p. 185°.

To ¼-in. layer of O.S. in a t.t. add 3 c.c. acetone, shake until solution is complete, then add 1 c.c. acetic anhydride. Allow to stand 2 min., then add 5 c.c. aq. NaOH in order to neutralise some of the acetic acid formed (the soln. should still be acid ; if not, just acidify with acetic acid), cool and shake.* Filter, wash the solid with cold water, then add it to 15 c.c. boiling water contained in a beaker. Stir, adding if necessary a few drops of glacial acetic acid, until solution is complete. Cool, filter, dry the solid and determine its m.p.

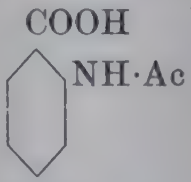
174° *m*-Aminobenzoic acid.



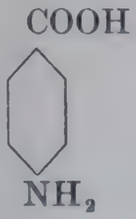
*Preparation of acetyl derivative*, m.p. 250°.

To ¼-in. layer of O.S. in a t.t. add 5 c.c. water and 1 c.c. acetic anhydride. Close the mouth of the t.t. and shake vigorously for 2 min. Cool, then proceed as described under "*o*-Aminobenzoic acid," commencing at the asterisk.

185° Acetyl anthranilic acid.



186° *p*-Aminobenzoic acid.



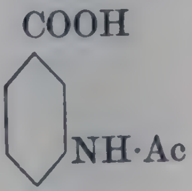
Proceed as indicated under "Acetyl derivatives of aromatic primary monamines" (page 200).

If (*a*) acetic acid is detected in the distillate, add to the residue in the flask just sufficient $NH_4OH$ to yield an alkaline soln. Acidify with glacial acetic acid, cool and shake. Filter off the solid, wash it with cold water, crystallise from water, dry, and determine the m.p.

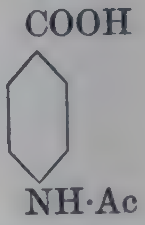
M.p. 144° indicates that the substance is anthranilic acid, and therefore O.S. is acetyl anthranilic acid.

(*b*) no acetic acid is detected in the distillate, confirm the identity of O.S. as *p*-aminobenzoic acid by preparing the acetyl derivative, m.p. 252°, in the manner described under "*m*-Aminobenzoic acid."

250° Acetyl *m*-aminobenzoic acid.



252° Acetyl *p*-aminobenzoic acid.



Follow the procedure under "Acetyl anthranilic acid" when a positive test for acetic acid will be obtained.

If the pptd. substance melts at

(*a*) 174° this indicates that it is *m*-aminobenzoic acid and therefore O.S. is acetyl *m*-aminobenzoic acid.

(*b*) 186° this indicates that it is *p*-aminobenzoic acid and therefore O.S. is acetyl *p*-aminobenzoic acid.

## Acetyl derivatives of aromatic primary monamines

Procedure for the identification of the acetyl derivatives whose m.p.s are listed on pages 187 and 217.

(*a*) In a 100-c.c. wide-mouthed flask place 1 g. of O.S., 10 c.c. conc. HCl, 5 c.c. water and some porous pot. Heat the contents of the flask to boiling under a reflux condenser and continue boiling for 5 min.

If (i) the hydrochloride of the amine has separated out as a solid, cool and filter. Test the filtrate for the presence of acetic acid in the manner described on page 68. If O.S. is an acetyl derivative a positive result will be obtained. Wash the solid with cold water, then add it to 50 c.c. boiling water contained in a beaker. Continue boiling with stirring until solution is complete, then cool. Add 10 c.c. aq. NaOH, cool and stir well. Filter off the pptd. amine, wash it well with cold water, dry, and determine the m.p.

| M.p. | |
|---|---|
| 50° | indicates that O.S. is acetyl α-naphthylamine. |
| 112° | ,, ,, ,, ,, acetyl β-naphthylamine. |

(ii) no solid hydrochloride has separated, continue boiling for 10 min., then distil until 7–8 c.c. of distillate is obtained. Test the distillate for the presence of acetic acid in the manner described on page 68. If O.S. is an acetyl derivative a positive result will be obtained.

In order to distinguish between two or more acetyl derivatives with m.p.s close together, or for further confirmation of the identity of O.S., proceed as indicated under (*b*).

(*b*) Add to the contents of the flask aq. NaOH until the mixture is alkaline, cool and shake. Prepare a benzoyl derivative of the liberated amine by adding 2 c.c. benzoyl chloride, etc., as described on page 217. Determine the m.p. and refer to the following appropriate list (according to whether halogen is absent or present) of m.p.s of benzoyl derivatives.

### Benzoyl derivatives of aromatic primary monamines.

$$R\text{—}NH\cdot CO\cdot C_6H_5.$$

*Halogen absent.*

If the determined m.p. is near to two of those given below, obtain (or prepare from the amine as described on page 217) one of these benzoyl derivatives and carry out a mixed m.p. determination (see page 14).

| M.p. | | |
|---|---|---|
| 64° | Benzoyl | *o*-anisidine. |
| 125° | ,, | *m*-toluidine. |
| 140° | ,, | 2-amino-*p*-xylene. |
| 143° | ,, | *o*-toluidine. |
| 154° | ,, | *p*-anisidine. |
| 158° | ,, | *p*-toluidine. |
| 163° | ,, | aniline (Benzanilide). |
| 173° | ,, | *p*-phenetidine. |
| 192° | ,, | 4-amino-*m*-xylene. |

*Cl present.*

| M.p. | |
|---|---|
| 100° | Benzoyl *o*-chloroaniline (*o*-Chlorobenzanilide). |
| 120° | ,, *m*- ,, (*m*- ,, ) |
| 192° | ,, *p*- ,, (*p*- ,, ). |

*Br present.*

| M.p. | |
|---|---|
| 202° | Benzoyl *p*-bromoaniline (*p*-Bromobenzanilide). |

## Anilides

Anilides of formic, acetic, propionic, and benzoic acids are included in Section 3 (page 189). The anilides included in this section are those detected by the azo dye test after hydrolysis in Test 9*B* (page 171).

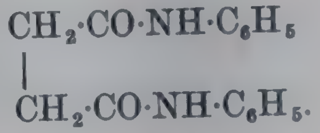
*Procedure :—*

Determine the m.p. of O.S. and refer to the following list of m.p.s. If one of these m.p.s is identical with, or near to, that of O.S., confirm the identity of O.S. by following the given procedure.

For m.p.s of other anilides see under the carboxylic acid detected in Test 9*B*.

M.p.

226° Succinanilide.



$$\begin{array}{l} CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_5 \\ | \\ CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_5. \end{array}$$

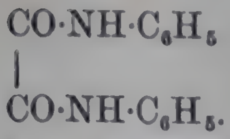
To R.G. of O.S. in a dry t.t. add twice the bulk of resorcinol and 2 drops conc. $H_2SO_4$. Gently heat until the mixture is a red-brown colour. Cool, add a few drops of water, then add aq. NaOH until the mixture is alkaline. Pour 1 c.c. of the alkaline soln. into a t.t. and fill up with water,—yellow-green fluorescence.

238° Carbanilide (Diphenylurea). $(C_6H_5{\cdot}NH)_2CO$.

*Preparation of acetanilide*, m.p. 114°.

In a 100-c.c. wide-mouthed flask place 1 g. of O.S. and 2½ c.c. each of acetic anhydride and glacial acetic acid. Heat to boiling under a reflux condenser and continue boiling for 15 min., periodically loosening the condenser clamp and giving the flask a rotary movement. Add 30 c.c. boiling water, boil for 1–2 min., then filter. Cool, filter off the crystals, recrystallise them from dilute acetic acid, dry, and determine the m.p.

M.p.
245° Oxanilide.



$$\begin{array}{l} CO\cdot NH\cdot C_6H_5 \\ | \\ CO\cdot NH\cdot C_6H_5. \end{array}$$

(*a*) To $\frac{1}{8}$-in. layer of O.S. in a dry t.t. add 5 drops conc. $H_2SO_4$. Gently warm the mixture by rotating the end of the tube over a small flame, and turn the mouth of the tube periodically to the flame. CO is evolved and burns with a characteristic blue flame.

(*b*) In a 100-c.c. wide-mouthed flask place 1 g. solid KOH, 5 c.c. water, 5 c.c. alcohol and the equivalent of $\frac{1}{8}$-in. layer in a t.t. of O.S.

Heat to boiling under a reflux condenser and continue boiling for 5 min. To 2 c.c. of the liquid from the flask add glacial acetic acid until the soln. is acid, then add 2–3 drops aq. $CaCl_2$,
—white ppt. (Ca oxalate.)

## Aminophenols

(Only hydrochlorides and sulphates of *p*-aminophenol, 2 : 4-diaminophenol, and *p*-methylaminophenol are here considered. These compounds will have been indicated by the deep red or deep brown soln. obtained on shaking them with aq. NaOH.)

*Procedure for the identification of O.S.*

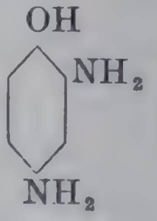
To 5 c.c. water add R.G. of O.S. and shake or heat until solution is complete. Add to the cold soln. one drop of aq. $FeCl_3$ and note any colour produced immediately, or within 15 sec.

If (*a*) an immediate wine-red colour is obtained, apply the tests under "Amidol."

(*b*) a deep violet colour develops within 15 sec., proceed as indicated under "Salts of *p*-aminophenol."

(*c*) neither of the results described under (*a*) and (*b*) is obtained, apply the tests under "Metol."

*Amidol* (Hydrochloride or sulphate of 2 : 4-diaminophenol,

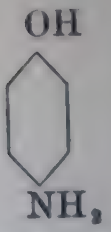


).

(*a*) Dissolve R.G. of O.S. in 5 c.c. cold water. Add the soln. to 2 c.c. aq. $AgNO_3$,
—deep red colour (with ppt. of AgCl if O.S. is a hydrochloride).

(*b*) Add R.G. of O.S. to 2 c.c. limewater and shake,
—yellow soln., rapidly changing to deep blue.

*Salts of* p-*aminophenol*,



(*a*) Dissolve R.G. of O.S. in 20 c.c. water. To 5 c.c. of the cold soln. add 1 c.c. aq. NaOH and 1 c.c. of saturated aq. phenol soln.; shake,
—deep blue colour develops in about 1 min.

(*b*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. dichromate mixture and heat to boiling,
—pungent odour of *p*-benzoquinone.

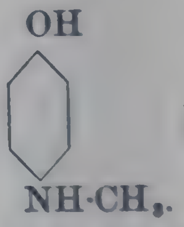
(*c*) *Preparation of quinonechloroimide*, m.p. 85°.

To $\frac{1}{4}$-in. layer of O.S. in a t.t. add 5 c.c. dil. HCl, warm or shake until solution is complete. To the cold soln. add 5 c.c. conc. NaOCl soln. and shake. Filter off the yellow ppt., wash it well with cold water, dry, and determine the m.p.

(*d*) *Preparation of diacetyl derivative of* p-*aminophenol*, m.p. 150°.

To $\frac{1}{2}$-in. layer of O.S. in a t.t. add 3 c.c. acetic anhydride, heat to boiling and continue boiling with shaking for 1 min. Cool, add 5 c.c. water and shake. Filter, wash the solid with cold water, dry, and determine the m.p.

*Metol* (*Sulphate of* p-*methylaminophenol*, ).



(*a*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. dil. HCl and shake until solution is complete. Add 2 c.c. of $2\frac{1}{2}\%$ aq. $NaNO_2$ and shake,
—ppt. of pale-yellow, matted needles of nitrosamine, (m.p. 136°). Treat the mixture in the manner described for the emulsion under "Secondary amines" (page 206), when a positive test for a nitrosamine will be obtained.

(*b*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. dichromate mixture and heat to boiling,
—pungent odour of *p*-benzoquinone.

(*c*) *Preparation of monoacetyl derivative of* p-*methylaminophenol*, m.p. 240°.

To $\frac{1}{4}$-in. layer of O.S. in a t.t. add 10 c.c. water and shake until solution is complete. Add 2 c.c. acetic anhydride and shake vigorously until crystals separate. Filter, wash the solid with water, dry, and determine the m.p.

Dibenzoyl derivative of *p*-methylaminophenol, m.p. 175°. (For method of preparation see page 217).

## *SECTION 4*

# *COMPOUNDS YIELDING A WHITE OR YELLOW EMULSION WITH DIL. HCl AND AQ. $NaNO_2$*

*Procedure :—*

Heat 2 c.c. of Fehling's soln. (equal volumes of No. 1 and No. 2) to boiling and add a drop or R.G. of O.S.

If no change occurs see "Secondary amines" (page 206).

Immediate reduction (i.e. the disappearance of the blue colour, and the production of a red ppt. of $Cu_2O$) indicates that O.S. is a hydrazine derivative. (Only phenylhydrazine $C_6H_5{\cdot}NH{\cdot}NH_2$ and its hydrochloride are here considered. As usually met with phenylhydrazine is a yellow or brownish oily liquid or crystalline mass, which yields a ppt. of hydrochloride on adding to dil. HCl, and a ppt. of oxalate on adding to aq. oxalic acid. The salts yield an acid aq. soln.)

Confirm the identity of the base by preparing benzaldehyde phenylhydrazone, m.p. 153°–156°, as follows :—

If O.S. is

(*a*) the free base, to 2 c.c. of 50% acetic acid add 5 drops of O.S., heat just to boiling, add 5 drops of benzaldehyde and shake.

Add 5 c.c. water, shake vigorously and cool. Filter, etc., as indicated below.

(*b*) a hydrochloride, to $\frac{1}{8}$-in. layer of O.S. in a t.t. add an equal bulk of crystallised sodium acetate and 5 c.c. water. Heat until solution is complete, then add 5 drops of benzaldehyde, shake vigorously and cool.

Filter off the solid phenylhydrazone and wash it with cold water. Crystallise the phenylhydrazone twice from alcohol, dry a thin layer on filter paper over a small flame, and determine the m.p.

### Secondary amines

The yellow or white emulsion obtained by the action of dil. HCl and aq. $NaNO_2$ on a soln. of O.S. consists of an insoluble nitrosamine, formed from a secondary amine.

Confirm the presence of a nitrosamine as follows :—

Pour the emulsion into a small separating funnel and add the equivalent of $\frac{1}{4}$-in. layer in a t.t. of urea (to destroy excess of $HNO_2$). Leave the funnel unstoppered, shake round and allow to stand for 5 min. Add 5 c.c. ether, shake and allow to stand until two well-defined layers are formed. Run off the lower layer, and wash the ethereal soln. with successive quantities of water (3 c.c.) until the lower layer, after running off, gives no blue colour on the addition of starch iodide soln. Separate as much water as possible from the ethereal soln. Pour 2 drops of the latter through the neck of the funnel into a dry t.t. and add 5 drops conc. $H_2SO_4$. A deep blue colour indicates that O.S. is diphenylamine or one of its salts; see under "O.S. solid" (page 208). If no blue colour is obtained add R.G. of phenol and rotate the tube to mix the contents. A green or blue-green colour, turned violet-red with a drop of water, and blue on adding aq. NaOH until the mixture is alkaline, indicates a nitrosamine. (Liebermann's reaction.)

**Identification of O.S.**

Follow the appropriate procedure, i.e. under "O.S. liquid" (below) or under "O.S. solid" (page 207).

***O.S. liquid.***

(Methylaniline, b.p. 192°, and ethylaniline, b.p. 206°, only are here considered.)

To 1 c.c. of O.S. add 2 c.c. acetic anhydride and one drop of conc. $H_2SO_4$ and allow to stand 5 min. Add 10 c.c. water, then add conc. $NH_4OH$ until the liquid is just alkaline, cool and stir.

If (*a*) solid separates, filter it off, dissolve it in 10 c.c. boiling 5% acetic acid; cool. Filter off the crystals, dry, and determine the m.p.

M.p. 101° indicates that O.S. is methylaniline,

$$C_6H_5{\cdot}NH{\cdot}CH_3,$$

(The acetyl derivative of ethylaniline melts at 54° and when prepared in the above manner usually remains as an oil.) Confirm the identity of O.S. by the preparation of the *p*-toluenesulphonyl derivative. m.p. 94° (see page 218).

(*b*) no solid separates, to 1 c.c. of O.S. add 10 c.c. of a saturated soln. of picric acid in benzene and stir. Filter, wash the solid picrate carefully with benzene, crystallise from aqueous alcohol, dry, and determine the m.p.

M.p. 137° indicates that O.S. is ethylaniline,

$$C_6H_5{\cdot}NH{\cdot}Et.$$

***O.S. solid.***

If the aq. soln. of O.S. is definitely acid, proceed as under **B** (page 209), otherwise as under **A** (page 208).

**A. Aq. soln. of O.S. not acid.**

Apply the test given, or prepare the derivative indicated under the name of the secondary amine whose m.p. is identical with, or near to, that of O.S.

M.p.

37° Benzylaniline, $C_6H_5\cdot NH\cdot CH_2\cdot C_6H_5$. (Hydrochloride sparingly soluble.)

Benzoyl derivative, m.p. 107° (see page 217).

54° Diphenylamine. $(C_6H_5)_2NH$.

Add R.G. of O.S. to 1 c.c. cold conc. $H_2SO_4$ and shake, —O.S. dissolves.

To the soln. add one drop of 2½% aq. $NaNO_2$, —deep blue colour.

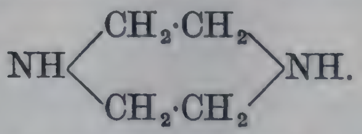
*Derivatives of diphenylamine.*

*Preparation of acetyl derivative*, m.p. 101°.

In a 100-c.c. wide-mouthed flask place 1 g. of O.S. and 2 c.c. each of acetic anhydride and glacial acetic acid. Fit the flask with a reflux condenser, heat the contents to boiling and continue boiling for 15 min.

Allow the contents of the flask to cool somewhat, add 20 c.c. water, heat to boiling and gradually add glacial acetic acid until all the oil is in solution. Cool and stir, then filter. Recrystallise the solid from aqueous alcohol, dry, and determine the m.p.

*Benzoyl diphenylamine*, m.p. 179°. (The preparation of this derivative is not convenient for identification purposes, since it necessitates boiling with benzoyl chloride in toluene soln. for some considerable time.)

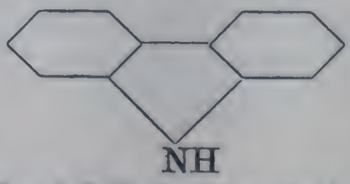
104° Piperazine, 

$NH\left\langle\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\right\rangle NH$.

(Forms a hydrate, m.p. 44°. Readily soluble in water; aq. soln. strongly alkaline.)

Apply Simon's test for a soluble secondary amine (page 213), using 2 R.G. of O.S., when a positive result will be obtained.

Dibenzoyl derivative, m.p. 191° (see page 217).

238° Carbazole.  (Insoluble in dil. HCl.)

Add R.G. of O.S. to 1 c.c. cold conc. $H_2SO_4$ and shake, —O.S. dissolves yielding a deep yellow soln.

To the soln. add one drop of $2\frac{1}{2}\%$ aq. $NaNO_2$,
—deep green colour.
Picrate (orange), m.p. 182° (see page 53).

### B. Aq. soln. of O.S. definitely acid.

A salt of an aromatic secondary amine is indicated. (Only halide salts, sulphates, and oxalates of methylaniline, ethylaniline, benzylaniline, and diphenylamine are here considered.)

If no acid radical has been detected apply the following test :—
Dissolve R.G. of O.S. in 2 c.c. boiling 50% acetic acid and add 2–3 drops aq. $CaCl_2$. A white ppt. indicates an oxalate.

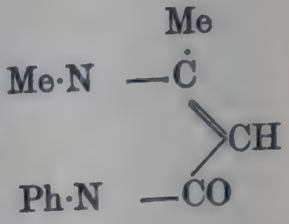
*Identification of the amine.*

In the case of a diphenylamine salt the amine will have been already detected; diphenylamine, owing to its weak basic character, may be liberated by boiling the salt with water, and its identity may be confirmed by filtering it off, washing with water, drying, and determining the m.p. (54°). In the case of a salt of any other amine, isolate the base in the manner described under "Salts of aromatic primary monamines" (page 198) and identify it in the manner indicated under "O.S. liquid" (page 207) or under "O.S. solid" (page 207).

## *SECTION 5*

# *COMPOUNDS YIELDING A GREEN, VIOLET-BLUE, OR RED-BROWN COLOUR WITH DIL. HCl AND AQ. NaNO$_2$*

*Green colour* indicates **Antipyrin (Phenazone)**

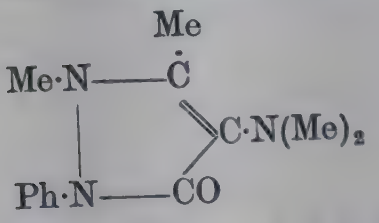


m.p. 111°–113°.

(*a*) Dissolve R.G. of O.S. in 2 c.c. water. To the cold soln. add 1 drop aq. FeCl$_3$,
—red-brown colour.

(*b*) Dissolve R.G. of O.S. in 2 c.c. water. Add the cold soln. to 2 c.c. Br. water,
—ppt. formed which on shaking dissolves to a colourless soln.

*Violet-blue colour*, with evolution of gas, becoming yellow on heating, indicates **Amidopyrin (Pyramidon)**



m.p. 107°–109°.

(*a*) To ⅛-in. layer of O.S. in a t.t. add 2 c.c. dil. H$_2$SO$_4$, warm until solution is complete, then cool. Add 2 drops aq. FeCl$_3$,
—violet-blue colour.

(*b*) Dissolve R.G. of O.S. in 2 c.c. water. To the cold soln. add 2 c.c. aq. AgNO$_3$,
—deep violet colour develops in about ½ min.; the soln. then becomes opaque owing to the formation of a grey ppt. of Ag.

*Red-brown ppt. or colour.*

After the mixture has stood for at least 5 min. add 10 c.c. aq. NaOH.

If (*a*) the mixture is dark brown, see "*m*-Diamines."

(*b*) a yellow-green ppt. is obtained, cool, add 3 c.c. ether, cork the tube and invert two or three times.

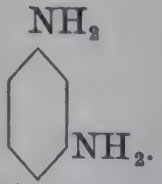
A green ethereal layer indicates that a *p*-nitroso-compound is present. See "Dialkylanilines" (page 211).

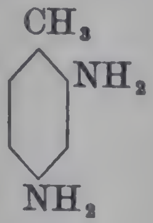
***m*-Diamines.** (*m*-Phenylenediamine: *m*-Tolylenediamine. Colourless when pure; darken rapidly in the air.)

*If the aq. soln. of O.S. is not acid*, a free base is indicated; identify by m.p. and by the preparation of a derivative (see list of *m*-diamines below).

*If the aq. soln. of O.S. is definitely acid*, a salt is indicated (hydrochlorides and sulphates only are considered). For identification of the base prepare a benzoyl derivative (see page 217).

M.p.

63° *m*-Phenylenediamine,  Dibenzoyl derivative, m.p. 240°. Diacetyl, m.p. 191°.

99° *m*-Tolylenediamine,  Dibenzoyl derivative, m.p. 224°. Diacetyl, m.p. 224°.

(For preparation of derivatives, see page 217.)

**Dialkylanilines** (Dimethylaniline, b.p. 192°, diethylaniline, b.p. 213°).

***O.S. liquid.***

To ¼-in. layer of powdered oxalic acid in a t.t. add 5 c.c. alcohol, heat until solution is complete, then cool. Add 1 c.c. of O.S. and shake.

*If a white ppt. is formed* in a few seconds, filter, wash the solid with alcohol, dry, and determine the m.p. M.p. 139° indicates that the ppt. is the acid oxalate of dimethylaniline, $C_6H_5{\cdot}N(CH_3)_2$.

*If no ppt. is obtained*, add 1 c.c. of O.S. to 5 c.c. of a saturated soln. of picric acid in benzene, cool, and scrape the glass in contact with the liquid with a glass rod in order to assist crystallisation. Filter, carefully wash the solid with alcohol, crystallise from alcohol, dry, and determine the m.p. M.p. 142° indicates that the picrate is that of diethylaniline, $C_6H_5{\cdot}N(Et)_2$.

***O.S. solid.*** *Aq. soln. definitely acid.*

A salt is indicated. If no acid radical has been detected, apply the following test :—Dissolve R.G. of O.S. in 2 c.c. boiling 50%

acetic acid and add 2–3 drops aq. $CaCl_2$. A white ppt. indicates an oxalate.

*To identify the base*, boil 2 g. of O.S. with 10 c.c. dil. HCl until solution is complete, cool and pour the soln. into a separating funnel. Add 10 c.c. of 20% aq. KOH and extract with 10 c.c. ether (see page 21). Distil off the ether and add to the residue in the flask 5 c.c. of a saturated soln. of picric acid in benzene. Cool, and scrape the glass in contact with the liquid with a glass rod in order to assist crystallisation. Filter, carefully wash the solid picrate with alcohol, crystallise from alcohol, dry, and determine the m.p.

M.p. 142° indicates that O.S. is a salt of diethylaniline.
,, 163° ,, ,, ,, ,, dimethylaniline.

## SECTION 6

# ALIPHATIC AND HETEROCYCLIC AMINES

*Procedure for the identification of O.S.:—*

Determine the b.p. and refer to the following appropriate list (i.e. according to whether O.S. is miscible with water, or sinks in water) of b.p.s of amines. If one of these b.p.s is identical with, or near to, that of O.S., confirm the identity of O.S. by applying to it any tests given, and by preparing and determining the m.p. of one or more of the derivatives there indicated. For methods of preparation of derivatives (if not given under the amine), see page 215.

**O.S. miscible with water.**

B.p.

55° Diethylamine. $(C_2H_5)_2NH$. Ammoniacal, fishy odour.

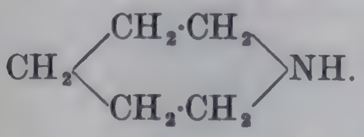
*Simon's test for a secondary amine.*

Prepare a soln. of acetaldehyde as follows: Wind one end of a piece of stout copper wire, about 8 in. long, six times round a glass rod so as to form a close spiral. Hold the straight end of the wire by means of tongs, and heat the spiral in a flame until the metal becomes coated with the black oxide. Plunge the red-hot spiral into 3 c.c. of alcohol contained in a t.t. Withdraw the spiral, cool the liquid, and repeat the process twice.

Add one drop of O.S. to 2 c.c. of ½% aq. sodium nitroprusside, then add 1 c.c. of the freshly prepared soln. of acetaldehyde,

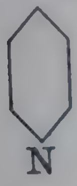
—deep blue colour develops in a few secs.

*p*-Toluenesulphonyl derivative, m.p. 60°. *m*-Nitrobenzenesulphonyl derivative, m.p. 66°. Compound with phenyl *iso*cyanate, m.p. 85°.

105° Piperidine.  Ammoniacal, unpleasant odour. (Fumes in the air, owing to the formation of carbonate.)

Apply Simon's test under "Diethylamine," when a similar result will be obtained.

*p*-Toluenesulphonyl derivative, m.p. 100°. Benzenesulphonyl derivative, m.p. 93°. Picrate, m.p. 151°. Compound with phenyl *iso*cyanate, m.p. 171°.

115° Pyridine.  Unpleasant odour.

Gives no blue colour in Simon's test. (Distinction from piperidine.)

(*a*) Add a drop of O.S. to 2 c.c. aq. $HgCl_2$, —immediate white ppt. of pyridine mercurichloride.

(*b*) To 2 c.c. dil. HCl add one drop of O.S., then add Mayer's reagent (see page 244), drop by drop. A permanent, pale yellow ppt. is obtained after the addition of about 5 drops of the reagent; the ppt. dissolves on heating and separates again on cooling.

(*c*) Into a dry t.t. pour one drop each of O.S. and methyl iodide,—soln. becomes yellow and cloudy. Warm slightly—vigorous reaction occurs, and a clear yellow liquid is obtained, which, on cooling, forms a crystalline mass of pyridine methiodide (m.p. 117°).

Add R.G. of solid KOH and heat, —brown oil distils and condenses on the sides of the tube, odour very disagreeable.

Picrate, m.p. 164°.

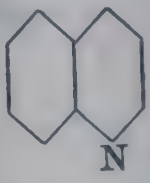
116° Ethylenediamine. $CH_2{\cdot}NH_2$ Ammoniacal odour.
$CH_2{\cdot}NH_2$

Gives no ppt. with aq. $HgCl_2$ or Mayer's reagent (Distinction from pyridine.)

Apply Test 4 (page 168) when an evolution of gas (N will be observed.

Di-*p*-toluenesulphonyl derivative, m.p. 160°.

**O.S. sinks in water.**

B.p.
238° Quinoline.  Characteristic odour.

Gives no reaction with nitrous acid in Test 4 (pag 168).

(*a*) To 2 c.c. dil. HCl add one drop of O.S., then add one drop of Mayer's reagent (see page 244),
—immediate, pale yellow ppt., which dissolves on heating and separates again on cooling.

(*b*) To 2 c.c. dil. HCl add one drop of O.S., then add one drop of a soln. of iodine in KI,
—immediate, red-brown ppt.

(*c*) *Preparation of quinoline tartrate*, m.p. 126°.

To ¼-in. layer of powdered tartaric acid in a t.t. add 5 c.c. water, and shake until solution is complete. Add ½ c.c. of O.S. and shake or stir until solid separates. Filter, wash the solid with alcohol, crystallise from a small quantity of water, dry, and determine the m.p.

(*d*) *Preparation of quinoline dichromate.* (Orange-yellow.)

To ¼-in. layer of powdered $K_2Cr_2O_7$ in a t.t. add 5 c.c. dil. HCl, heat until soln. is complete, then cool.

Add ½ c.c. of O.S. and shake,
—orange ppt. (The salt may be recrystallised from water, m.p. about 165°. Darkens near m.p.)

Picrate, m.p. 203°.

## METHODS OF PREPARATION OF THE DERIVATIVES INDICATED IN THE FOREGOING LISTS OF AMINES

(See sections on "Crystallisation," and "Drying of substances," pages 16–21.)

**p Toluenesulphonyl derivatives.**

See page 218.

**Benzenesulphonyl, or *m*-nitrobenzenesulphonyl derivatives.**

Follow the procedure given on page 218 for the preparation of *p*-toluenesulphonyl derivatives, using the appropriate sulphonyl chloride.

**Compounds with phenyl *iso*cyanate.**

To a soln. of ½ c.c. of phenyl *iso*cyanate in 10 c.c. dry petroleum ether add, drop by drop, ½ c.c. of O.S. Filter off the white ppt., which is formed immediately, and wash it well with petroleum ether. Dry, and determine the m.p.

**Picrates.**

To 10 c.c. of a cold saturated soln. of picric acid in benzene add 1 c.c. of O.S. and stir. Filter and wash the solid carefully with benzene. Crystallise pyridine and quinoline picrates from alcohol (quinoline picrate is sparingly soluble in alcohol and also in benzene), and piperidine picrate from water.

### Salts of aliphatic and heterocyclic amines.

On the addition of aq. NaOH the amines are liberated, the lower aliphatic ones possessing ammoniacal, fishy odours. The vapour of an aliphatic primary monamine, and also that of dimethylamine, may be distinguished from ammonia by giving a positive result in the following test :—To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. aq. NaOH and heat, meanwhile holding a roll of filter paper, the end of which has been moistened with an alcoholic soln. of 2 : 4-dinitrochlorobenzene ($\frac{1}{8}$-in. layer of the solid in a t.t. dissolved in 5 c.c. alcohol) in the mouth of the tube—paper coloured intensely yellow. (With ammonia no yellow colour is produced ; with diethylamine or ethylenediamine only a faint colour is obtained.) Identify the amine, if possible, in the manner described under *A* ; also see under *B*.

*A.* Follow the procedure given for secondary amines under "*p*-Toluenesulphonyl derivatives" (page 218).

If (*a*) a *p*-toluenesulphonyl derivative is obtained,

M.p.

60° indicates that O.S. is a salt of diethylamine, $(C_2H_5)_2NH$ (b.p. 55°).

79° indicates that O.S. is a salt of dimethylamine, $(CH_3)_2NH$ (gas).

100° indicates that O.S. is a salt of pipéridine (heterocyclic), b.p. 105°.

(*b*) no derivative is obtained, follow the procedure for primary amines.

If (i) a *p*-toluenesulphonyl derivative is obtained,

M.p.

62° indicates that O.S. is a salt of ethylamine, $C_2H_5{\cdot}NH_2$ (b.p. 18°).

77° indicates that O.S. is a salt of methylamine, $CH_3{\cdot}NH_2$ (gas).

160° indicates that O.S. is a salt of ethylenediamine (b.p. 116°).

(ii) no derivative is obtained, this indicates that O.S. is a salt of a tertiary amine. (Trimethylamine is an inflammable gas with a very fishy odour ; triethylamine is a liquid, b.p. 89°.)

*B.* On the addition of a conc. aq. soln. of $NaNO_2$ to a soln. of the salt in dil. HCl, primary amines yield an alcohol with a rapid effervescence of nitrogen, whereas secondary amines yield an oily nitrosamine (for detection proceed as indicated under

"Secondary amines," page 206). With tertiary amines there is no apparent reaction.

## GENERAL METHODS OF PREPARATION OF DERIVATIVES OF PRIMARY AND SECONDARY AMINES

(See sections on "Crystallisation," and "Drying of substances," pages 16–21).

**Acetyl derivatives of primary amines.** (Special methods for the preparation of acetyl derivatives of secondary amines are given under the individual amine.)

To 1 c.c. or 1 g. of O.S. in a t.t. add 2 c.c. acetic anhydride; if O.S. is solid, warm and shake until solution is complete. Cool, pour into 10 c.c. water, and stir until the oil solidifies. Filter, and wash the solid with cold water. Add the solid to 20–30 c.c. boiling water contained in a beaker and stir; if the solid does not dissolve completely gradually add glacial acetic acid with stirring until solution is complete. (Alcohol is a more suitable solvent for acetyl derivatives of the naphthylamines.) Cool, filter off the crystals, dry, and determine the m.p.

*M.p.s of acetyl derivatives of solid aromatic primary monamines.* (For m.p.s of acetyl derivatives of liquid aromatic primary monamines see page 187.)

*Halogen absent.*

| M.p. | |
|---|---|
| 127° | Acetyl *p*-anisidine. |
| 132° | ,, β-naphthylamine. |
| 148° | ,, *p*-toluidine. |
| 155° | ,, *m*-nitroaniline (*m*-Nitroacetanilide). |
| 159° | ,, α-naphthylamine. |
| 212° | ,, *p*-nitroaniline (*p*-Nitroacetanilide). |

*Cl present.*

| | |
|---|---|
| 178° | Acetyl *p*-chloroaniline (*p*-Chloroacetanilide). |

*Br present.*

| | |
|---|---|
| 167° | Acetyl *p*-bromoaniline (*p*-Bromoacetanilide). |

*M.p.s of acetyl derivatives of liquid aromatic secondary amines.*

| | |
|---|---|
| 54° | Acetyl ethylaniline (Ethylacetanilide). |
| 101° | Acetyl methylaniline (Methylacetanilide). |

**Benzoyl derivatives.**

(*a*) *From a free amine.*

In a 100-c.c. conical flask dissolve 1 c.c. or 1 g. of O.S. in 5 c.c. acetone. (See note.) Add 2 c.c. benzoyl chloride, then add 50 c.c. aq. NaOH (the first 10 c.c. or so gradually with cooling and shaking, then the remainder all at once);

cool. Cork the flask and shake vigorously for 10 min. (If time permits continue the shaking until the odour of the benzoyl chloride has practically disappeared.) Filter, wash the solid, first with dil. HCl, then with cold water, crystallise from alcohol, dry, and determine the m.p.

NOTE.

By the use of acetone a cleaner product is obtained, and the amine, especially if solid, is brought into more intimate contact with the acid chloride.

(*b*) *From a salt of an amine.*

In a 100-c.c. conical flask place 1 g. of O.S. and 10 c.c. aq. NaOH. Add 2 c.c. benzoyl chloride, etc., as described above under (*a*).

*M.p.s of benzoyl derivatives of aromatic primary monamines.* See page 201.

*M.p.s of benzoyl derivatives of aromatic secondary amines.*

| | |
|---|---|
| 63° | Benzoyl methylaniline. |
| 107° | ,, benzylaniline. |

**p-Toluenesulphonyl derivatives.**

In a 100-c.c. conical flask dissolve 2 g. of *p*-toluenesulphonyl chloride in 5 c.c. acetone, add 1 c.c. or 1 g. of O.S., and 30 c.c. aq. NaOH. Cork the flask and shake vigorously, more or less continuously, for 10 min.

If the amine is

(*a*) *primary*, filter and acidify the filtrate with conc. HCl. (If an oil separates, shake vigorously until it solidifies.) Filter off the solid, wash it well with cold water, dry, and determine the m.p.

(*b*) *secondary*, heat the contents of the flask to boiling, and continue boiling, shaking round frequently, for 5 min. in order to destroy the excess of sulphonyl chloride. Cool and add an equal volume of water. (If an oil is present shake vigorously until it solidifies.) Filter off the solid, wash it well with cold water, crystallise from aqueous alcohol, dry, and determine the m.p.

For m.p.s of *p*-toluenesulphonyl derivatives of the commoner aromatic primary and secondary amines see page 257, and for those of aliphatic amines see page 216.

## METHOD OF DETERMINATION OF THE EQUIVALENT WEIGHT OF AN AROMATIC AMINE

(1) Prepare the hydrochloride of the amine as follows:—

(A sulphate or oxalate is not suitable owing to the possibility of an acid salt being formed.)

**A.**

***O.S. liquid.***

To 1 c.c. of O.S. add 3 c.c. conc. HCl; stir and cool.

If (*a*) solid separates, filter it off, drain as dry as possible, then wash with alcohol to remove any trace of free amine, and dry rapidly. (See "Drying of substances," page 19. Hydrochlorides are apt to become discoloured on prolonged heating in a steam oven.)

(*b*) no solid separates, proceed as under **B.**

***O.S. solid.***

If O.S. has been identified as diphenylamine proceed as under **B**, otherwise as follows:—

Boil 1 g. of O.S. with sufficient dil. HCl to effect solution. Cool, filter, etc., as in (*a*) under "O.S. liquid."

**B.**

Dissolve 1 c.c. or 1 g. of O.S. in 5 c.c. petroleum ether. (In the case of diphenylamine use a suitable volume of dry methylated ether.) Pass in dry HCl gas until the hydrochloride separates. Filter, wash the hydrochloride with the solvent employed for dissolving the amine, and dry rapidly. (See "Drying of substances," page 19.)

(2) Weigh accurately a watch-glass, add about 0·5 g. of the hydrochloride and weigh again. Wash off the solid with distilled water into a beaker (250 c.c. or larger) or through a sufficiently large funnel into a 250-c.c. conical flask. Add 5 or 6 drops of phenolphthalein soln., and titrate with $\frac{N}{10}$ NaOH (standardised in the manner described on page 81) until a red colour, which persists for a minute, is obtained. (An emulsion, or a ppt., may be present, owing to the liberated amine.)

Calculate the weight of hydrochloride which would be neutralised by 1,000 c.c. of N. NaOH; the result will be the equivalent weight of the hydrochloride. To obtain the equiv. wt. of the amine, subtract the equiv. wt. of HCl, i.e. 36·46.

EXAMPLE.

37·55 × 0·103 c.c. of N. NaOH neutralised 0·5012 g. of a hydrochloride.

1,000 c.c. of N. NaOH would neutralise $\frac{0{\cdot}5012 \times 1000}{37{\cdot}55 \times 0{\cdot}103}$ g.

$= 129{\cdot}6$ g.

Therefore the equiv. wt. of the hydrochloride = 129·6.

Equiv. wt. of amine = 129·6—36·46

= 93·1. (Theory 93·06.)

## *SECTION 7*

# *NITRO, AZO AND AZOXY COMPOUNDS*

These will have been indicated by

(*a*) their yellow, orange, or red colour.

or (*b*) the production of an intense yellow, orange, red-brown, or red colour on treating with aq. NaOH.

or (*c*) reduction to a primary amino compound (—$NH_2$ in nucleus) with $SnCl_2$ and HCl. (Test 8*B*, page 171).

*Procedure for the identification of O.S.* :—

Determine the b.p. if liquid, or the m.p. if solid, and refer to the appropriate list (i.e. according to whether halogen is absent or present) of b.p.s, or m.p.s. If one of these b.p.s or m.p.s is identical with, or near to, that of O.S., confirm the identity of O.S. by applying to it any tests given, and by preparing and determining the m.p. of the derivatives there indicated. For methods of preparation of derivatives (unless given under the compound) see page 231.

If O.S. is not found to be identical with one of the compounds in the following lists see " Additional nitro compounds " (page 233).

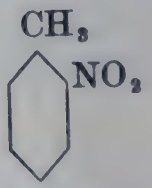
***O.S. liquid.***

**Halogen absent.**

B.p.

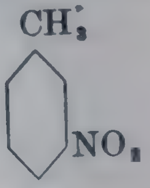
210° Nitrobenzene. $C_6H_5{\cdot}NO_2$. Bitter-almond odour.

*m*-Dinitrobenzene, m.p. 90°.

220° *o*-Nitrotoluene.  Bitter-almond odour.

2 : 4-Dinitrotoluene, m.p. 70°.

Oxidation → *o*-nitrobenzoic acid, m.p. 147°.

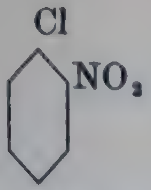
230° *m*-Nitrotoluene.  Faint bitter-almond odour.

Oxidation → *m*-nitrobenzoic acid, m.p. 141°.

**Cl present.**

B.p.

245° *o*-Nitrochlorobenzene.



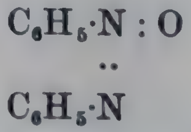
See under " O.S. solid," m.p. 32° (page 229).

***O.S. solid.***

**Halogen absent.**

M.p.

36° Azoxybenzene.

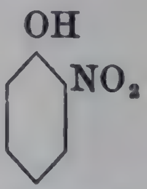


$$\begin{array}{c} C_6H_5{\cdot}N : O \\ \cdot\cdot \\ C_6H_5{\cdot}N \end{array}$$

Yellow.

Apply Test 8*B* (page 171) when a positive result will be obtained, owing to reduction of O.S. to aniline.

44° *o*-Nitrophenol.



Yellow. Tarry odour.

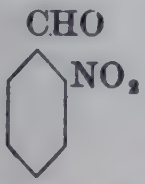
(*a*) To ⅛-in. layer of O.S. in a t.t. add 2 c.c. aq. NaOH and shake for ½ min.,—deep red soln.

(*b*) *Reduction to* o-*aminophenol*, identified by its benzoyl derivative, m.p. 182°.

In a 100-c.c. beaker place 1 g. of O.S., 10 c.c. aq. NaOH and 20 c.c. water. Heat to boiling, and add solid sodium hydrosulphite gradually until the soln. becomes colourless or pale yellow. Filter and cool. Filter off the crystals of *o*-aminophenol, wash them with cold water, and dry. Prepare the benzoyl derivative in the manner described on page 217, and determine its m.p.

(*o*-Nitrophenyl benzoate, m.p. 55°.)

44° *o*-Nitrobenzaldehyde.



Pale yellow.

Apply Test (*a*) under " *o*-Nitrophenol."

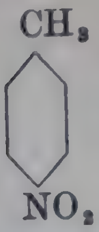
No change of colour occurs in the cold, but a red-brown soln. is obtained after boiling for ½ min.

Phenylhydrazone (deep red), m.p. 153°.

Oxidation → *o*-nitrobenzoic acid, m.p. 147°.

M.p.

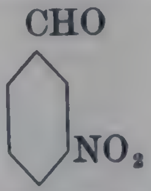
54° *p*-Nitrotoluene.



Pale yellow. Aromatic odour.

2 : 4-Dinitrotoluene, m.p. 70°.
Oxidation → *p*-nitrobenzoic acid, m.p. 238°.

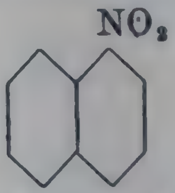
58° *m*-Nitrobenzaldehyde.



Pale yellow.

(Yields a yellow soln. on boiling with aq. NaOH.)
Phenylhydrazone (deep orange), m.p. 121°.
Oxidation → *m*-nitrobenzoic acid, m.p. 141°.

61° α-Nitronaphthalene.



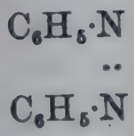
Yellow.

(*a*) Apply Test 8*B* (page 171) when a positive result will be obtained owing to reduction of O.S. to α-naphthylamine.

(*b*) To 2 c.c. conc. $H_2SO_4$ in a t.t. add R.G. of O.S. and shake,
—deep red soln.

Benzoyl α-naphthylamine, m.p. 160°.

68° Azobenzene.

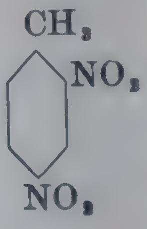


$$\begin{array}{c} C_6H_5{\cdot}N \\ \vdots \\ C_6H_5{\cdot}N \end{array}$$

Orange-red.

Apply Test 8*B* (page 171), when a brown-violet azo colour will be obtained. Hydrazobenzene is first formed by the reduction of O.S., and is converted by the HCl into benzidine. Test for the presence of benzidine hydrochloride in the reduction mixture by adding 1 c.c. dil. $H_2SO_4$ to 5 c.c. of the acid soln., when a white ppt. of benzidine sulphate will be obtained.

70° 2 : 4-Dinitrotoluene.



Colourless, or very pale yellow.

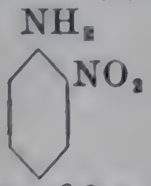
M.p.    (Gives a dark brown colour on boiling with aq. NaOH.)

(*a*) Dissolve R.G. of O.S. in 2 c.c. cold acetone and add one drop aq. NaOH,—deep blue colour, turned violet-red by acetic acid.

(*b*) *Reduction to 2-nitro-p-toluidine* (m.p. 72°) identified by its benzoyl derivative, m.p. 172°.

In a 100-c.c. wide-mouthed flask place 1 g. of O.S., 50 c.c. alcohol and 20 c.c. yellow $NH_4$ sulphide. Fit the flask with a reflux condenser, heat the contents to boiling and continue boiling for 10 min. Filter to remove pptd. sulphur. Cool the filtrate, pour it into a 250-c.c. separating funnel, add 100 c.c. water, and extract with 25 c.c. ether. Distil off the ether (see page 21) and from the residue prepare a benzoyl derivative in the manner described under "Benzoyl derivatives" (*a*), page 217.

71°  *o*-Nitroaniline.



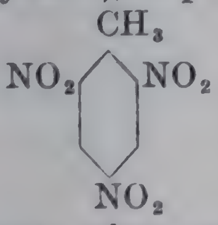
Orange.

To a mixture of 2 c.c. each of 2½% aq. $NaNO_2$ and dil. HCl add R.G. of O.S., shake and add to alkaline $\beta$-naphthol. (⅛-in. layer of $\beta$-naphthol in a t.t. dissolved in 5 c.c. aq. NaOH). —red ppt. of an azo colour.

Acetyl derivative (yellow), m.p. 92°.

Benzoyl derivative (yellow), m.p. 94°.

82°  2 : 4 : 6-Trinitrotoluene.



Pale yellow.

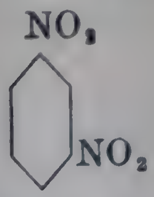
(Gives a deep red-brown colour on boiling with aq. NaOH.)

(*a*) Dissolve R.G. of O.S. in 2 c.c. cold acetone and add one drop aq. NaOH,—deep wine-red colour.

(*b*) *Preparation of compound with acenaphthene*, m.p. 109°.

Dissolve 0·23 g. of O.S. and 0·15 g. of acenaphthene separately in 5 c.c. hot alcohol. Mix the two solutions and cool. Filter off the solid, carefully wash it with alcohol, dry, and determine the m.p.

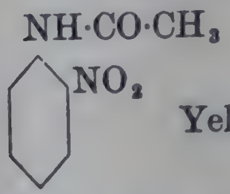
M.p.

90° *m*-Dinitrobenzene.  Very pale yellow.

(Gives a red-brown colour on boiling with aq. NaOH.)

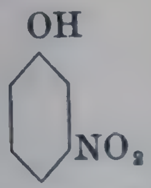
(*a*) Dissolve R.G. of O.S. in 2 c.c. cold acetone and add one drop aq. NaOH,
—violet-blue colour, turned violet-red by acetic acid.

(*b*) *Reduction to* m-*nitroaniline*, m.p. 114°.
Reduce in the manner described under "2 : 4-Dinitrotoluene" (*b*) (page 223), and after filtering to remove pptd. sulphur, add 100 c.c. water, and boil down to about $\frac{2}{3}$ of the volume. Filter to remove more pptd. sulphur, and cool the filtrate. Filter off the solid and recrystallise it from water. Dry, and determine the m.p.

92° *o*-Nitroacetanilide.  Yellow.

(*a*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. aq. NaOH and heat to boiling,
—orange soln., due to liberated *o*-nitroaniline.

(*b*) Hydrolyse to acetic acid and *o*-nitroaniline, m.p. 71°, in the manner described under "*p*-Nitroacetanilide" (page 228).
The distillate will be yellow, owing to *o*-nitroaniline passing over with the steam; the colour, however, will not interfere with the test for acetic acid.

96° *m*-Nitrophenol.  Yellow.

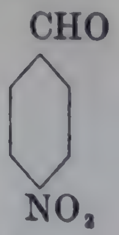
(*a*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. aq. NaOH and shake,
—orange-red soln.

(*b*) To 5 c.c. water in a t.t. add R.G. of O.S., heat to boiling with shaking, then cool.
Add 2 drops aq. $FeCl_3$,—violet-red colour.

Benzoate, m.p. 95°.

M.p.

106° *p*-Nitrobenzaldehyde. Very pale yellow.

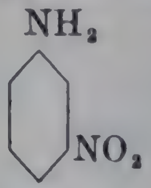


(Yields a deep red-brown soln. on boiling with aq. NaOH.)

Phenylhydrazone (red), m.p. 156°.

Oxidation → *p*-nitrobenzoic acid, m.p. 238°.

114° *m*-Nitroaniline. Golden yellow.



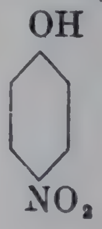
(*a*) Apply the test under "*o*-Nitroaniline" (page 223), when a similar result will be obtained.

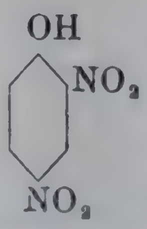
(*b*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add an equal bulk of zinc dust and 5 c.c. dil. HCl. Allow to stand for 5 min., shaking periodically, then filter. To the filtrate add 2 c.c. of 2½% aq. $NaNO_2$, —red-brown ppt., formed from the *m*-phenylenediamine obtained by reduction of O.S.

Acetyl derivative, m.p. 155°.

Benzoyl derivative, m.p. 155°.

114° { *p*-Nitrophenol. / 2 : 4-Dinitrophenol. } Pale yellow.





(Both yield an intense yellow colour with aq. NaOH.)

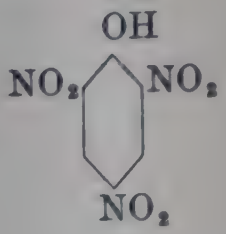
To 5 c.c. water in a t.t. add R.G. of O.S., heat to boiling with shaking, then cool. Add 2 drops aq. $FeCl_3$. A violet-red colour is obtained with *p*-nitrophenol but not with 2 : 4-dinitrophenol.

Acetyl derivative of *p*-nitrophenol, m.p. 81°.
" " " 2 : 4-dinitrophenol, m.p. 72°.
Benzoyl " " *p*-nitrophenol, m.p. 142°.
" " " 2 : 4-dinitrophenol, m.p. 132°.

M.p. *Confirmatory test for* p-*nitrophenol.*

Reduce in the manner described under "*o*-Nitrophenol" (page 221). To the aminophenol obtained apply the tests given under "Salts of *p*-aminophenol" (page 204).

122° Picric acid. (2 : 4 : 6-Trinitrophenol.)

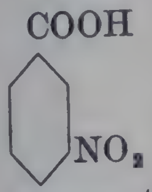


Light yellow.

(*a*) To 5 c.c. aq. NaOH add R.G. of O.S. and heat just to boiling. To the intense yellow soln. obtained add a drop of $NH_4$ sulphide,—deep red colour, due to the alkali salt of picramic acid, formed by the partial reduction of picric acid.

Naphthalene picrate, m.p. 149°. (See under "Naphthalene," page 123).

141° *m*-Nitrobenzoic acid.

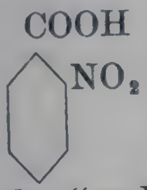


Colourless.

Grind together an amount of O.S. which would about half-fill the bulb of an ignition tube, and three times its bulk of dry soda-lime. Introduce the mixture into an ignition tube and heat,—bitter-almond-like odour of nitrobenzene.

Amide, m.p. 142°. Methyl ester, m.p. 79°. *p*-Nitrobenzyl ester, m.p. 141°.

147° *o*-Nitrobenzoic acid.

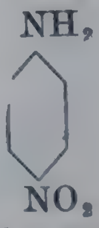


Colourless, or pale yellow.

Apply the test under "*m*-Nitrobenzoic acid," when a similar result will be obtained.

Amide, m.p. 174°. *p*-Nitrobenzyl ester, m.p. 111°.

147° *p*-Nitroaniline.



Yellow.

(*a*) Apply the test under "*o*-Nitroaniline" (page 223), when a similar result will be obtained.

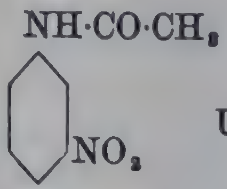
M.p.

(b) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add an equal bulk of zinc dust and 5 c.c. dil. HCl. Allow to stand for 5 min., shaking periodically, then filter. Apply the following test for *p*-phenylenediamine :—

Dilute the filtrate with water to 20 c.c. To 2 c.c. of this soln. add 2 c.c. aq. NaOH, 1 c.c. saturated aq. soln. of phenol and 1 c.c. conc. NaOCl soln.,—deep blue colour develops in about 1 min.

Acetyl derivative, m.p. 212°. Benzoyl derivative, m.p. 199°.

155° *m*-Nitroacetanilide.

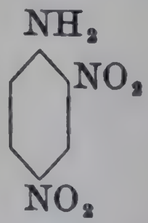


Usually light fawn.

(Gives a yellow colour on boiling with aq. NaOH due to liberated *m*-nitroaniline.)

Hydrolyse to acetic acid and *m*-nitroaniline (m.p. 114°) in the manner described under "*p*-Nitroacetanilide" (page 228).

176° 2 : 4-Dinitroaniline.



Yellow.

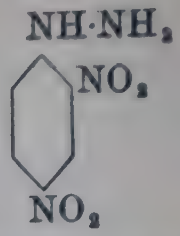
*Preparation of 2 : 4-dinitrophenol,* m.p. 114°.

In a 100-c.c. wide-mouthed flask place 1 g. of O.S., 20 c.c. of 20% KOH and some porous pot. Fit the flask with a reflux condenser, heat the contents to boiling and continue boiling for 15 min. Acidify with conc. HCl, cool, filter off the solid and wash it with cold water. Place the solid in the 100-c.c. flask, add 40 c.c. water, 10 c.c. conc. $H_2SO_4$ and some porous pot. Connect the flask to a condenser and distil until no more solid passes over, periodically adding boiling water to replace that removed by distillation. Pour water through the condenser in order to wash the solid into the receiver. Filter off the solid, wash it with cold water, dry, and determine the m.p.

Acetyl derivative, m.p. 121°.

M.p.

198° decomp. 2 : 4-Dinitrophenylhydrazine.



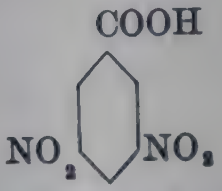
Red.

*Preparation of* m-*dinitrobenzene*, m.p. 90°.

In a 100-c.c. wide-mouthed flask place ½ g. of O.S., 50 c.c. of aq. $CuSO_4$ (Fehling's No. 1 soln.) and some porous pot. Fit the flask with a reflux condenser, heat the contents to boiling and continue boiling for 15 min. Disconnect the flask, attach it to a sloping condenser and distil until the volume of liquid in the flask has been reduced to about ⅓. Pour water through the condenser in order to wash the solid into the receiver. Filter off the solid, crystallise it from dilute alcohol, dry, and determine the m.p.

Acetone 2 : 4-dinitrophenylhydrazone, m.p. 126° (see page 65).

204° 3 : 5-Dinitrobenzoic acid.



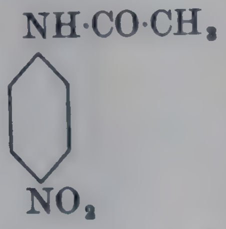
Pale yellow.

(Dissolves in cold aq. NaOH yielding a red-brown soln.).

Dissolve R.G. of O.S. in 2 c.c. cold acetone and add aq. NaOH, drop by drop, until the soln. is alkaline.
—deep blue colour.

Amide, m.p. 183°. Methyl ester, m.p. 107°. Ethyl ester, m.p. 93°.

212° *p*-Nitroacetanilide.



Pale yellow.

(Gives a yellow colour on boiling with aq. NaOH, due to liberated *p*-nitroaniline.)

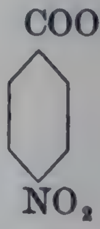
*Hydrolysis to acetic acid and* p-*nitroaniline*, m.p. 147°.

In a 100-c.c. wide-mouthed flask place 1 g. of O.S., 10 c.c. conc. HCl, 5 c.c. water and some porous pot. Fit the flask with a reflux condenser, heat the contents to boiling and continue boiling for

M.p.

10 min. Disconnect the flask, attach it to a sloping condenser and distil until 7–8 c.c. of distillate is obtained. Test the distillate for the presence of acetic acid in the manner described on page 68, when a positive result will be obtained. To the residue in the flask add 20 c.c. aq. NaOH and shake round. Cool, filter off the nitroamine, wash it with cold water, crystallise from water, dry, and determine the m.p.

238° *p*-Nitrobenzoic acid.



Colourless.

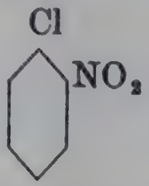
Apply the test under "*m*-Nitrobenzoic acid" (page 226) when a similar result will be obtained.

Amide, m.p. 201°. Methyl ester, m.p. 96°.
Ethyl ester, m.p. 57°. *p*-Nitrobenzyl ester, m.p. 168°.

**Cl present.**

M.p.

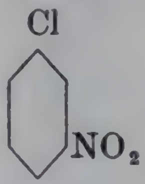
32° *o*-Nitrochlorobenzene.



Pale yellow.

2 : 4-Dinitrochlorobenzene, m.p. 50°.

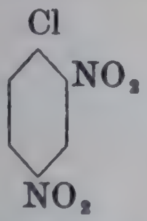
44° *m*-Nitrochlorobenzene.



Pale yellow.

Benzoyl *m*-chloroaniline, m.p. 120°.

50° 2 : 4-Dinitrochlorobenzene.



Very pale yellow.

(Gives an orange colour on boiling with aq. NaOH.)

(*a*) Dissolve R.G. of O.S. in 2 c.c. cold acetone and add one drop aq. NaOH,
—violet-blue colour, turned violet-red with acetic acid.

(*b*) *Hydrolysis to 2 : 4-dinitrophenol*, m.p. 114°.

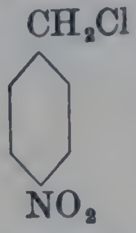
In a 100-c.c. wide-mouthed flask place 1 g. of O.S., 10 c.c. aq. NaOH and 10 c.c. water. Fit

M.p.

the flask with a reflux condenser, heat the contents to boiling and continue boiling for 15 min.; cool. Filter, acidify the filtrate with conc. HCl and cool. Filter off the solid, crystallise it from dil. HCl, dry, and determine the m.p.

Phenyl ether, m.p. 69° (see page 53).

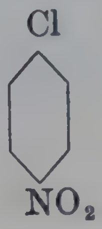
71° *p*-Nitrobenzyl chloride.



Very pale yellow.

*p*-Nitrobenzyl phenyl ether, m.p. 91°.
*p*-Nitrobenzyl benzoate, m.p. 89°.
Oxidation → *p*-nitrobenzoic acid, m.p. 238°.

83° *p*-Nitrochlorobenzene.

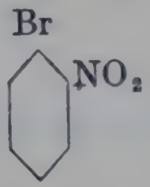


Pale yellow.

2 : 4-Dinitrochlorobenzene, m.p. 50°.

**Br present.**

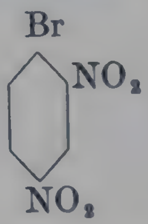
M.p.
41° *o*-Nitrobromobenzene.



Pale yellow.

2 : 4-Dinitrobromobenzene, m.p. 72°.

72° 2 : 4-Dinitrobromobenzene.



Pale yellow.

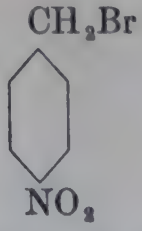
(Gives a yellow colour on boiling with aq. NaOH.)

(*a*) Dissolve R.G. of O.S. in 2 c.c. cold acetone and add one drop aq. NaOH,
—violet-red colour.

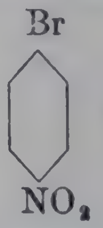
(*b*) *Hydrolysis to 2 : 4-dinitrophenol*, m.p. 114°.
Proceed as indicated under "2 · 4-Dinitrochlorobenzene" (*b*). (page 229).

Phenyl ether, m.p. 69° (see page 53).

M.p.

99° *p*-Nitrobenzyl bromide.  Pale yellow.

*p*-Nitrobenzyl phenyl ether, m.p. 91°.
*p*-Nitrobenzyl benzoate, m.p. 89°.
Oxidation → *p*-nitrobenzoic acid, m.p. 238°.

126° *p*-Nitrobromobenzene.  Practically colourless.

2 : 4-Dinitrobromobenzene, m.p. 72°.

## METHODS OF PREPARATION OF THE DERIVATIVES INDICATED UNDER THE NITRO COMPOUNDS IN THE FOREGOING LISTS

(See sections on "Crystallisation," and "Drying of substances," pages 16–21).

**Phenylhydrazones of nitrobenzaldehydes.**

Proceed as indicated under "Phenylhydrazones, O.S. solid" (page 65).

**Oxidation.**

*Nitrobenzaldehydes → nitrobenzoic acids.*

Follow the procedure under "Anisaldehyde," "Oxidation to anisic acid" (page 61), using 1 g. of O.S. Crystallise the ortho and meta compounds from water, and the para compound from alcohol.

*Nitrotoluenes and nitrobenzyl halides → nitrobenzoic acids.*

In a 100-c.c. wide-mouthed flask place 1 g. of O.S., 2½ g. solid $KMnO_4$, 40 c.c. water, 5 drops aq. NaOH and some porous pot. Fit the flask with a reflux condenser, and boil the contents until the purple colour of the $KMnO_4$ has disappeared. Cool, filter, and acidify the filtrate with conc. HCl. Filter off the solid and wash it with cold water. Crystallise the solid from water in the case of ortho and meta compounds, or from alcohol in the case of the para compound; dry, and determine the m.p.

**Dinitro compounds.**

m-*Dinitrobenzene ; 2 : 4-dinitrochlorobenzene ; 2 : 4-dinitrobromobenzene.*

Proceed as indicated under "Preparation of *m*-dinitrobenzene" (page 116). If O.S. is solid use 1 g. of it.

*2 : 4-Dinitrotoluene.*

Proceed as indicated under "Toluene" (page 116). If O.S. is solid use 1 g. of it.

**Benzoyl derivatives of nitrophenols and nitroamines.**

Proceed as indicated under "Benzoates" (page 52). In the case of *o*-nitrophenol and 2 : 4-dinitrophenol use aq. $Na_2CO_3$ instead of aq. NaOH (*o*-nitrophenyl benzoate usually only solidifies after standing for some time).

**Acetyl derivatives.**

(*a*) of nitrophenols.

Proceed as indicated under "Acetates" (page 52).

(*b*) of nitroanilines.

*Mononitroanilines.*

In a 100-c.c. wide-mouthed flask place 1 g. of O.S. and 5 c.c. acetic anhydride. Fit the flask with a reflux condenser, heat the contents to boiling and continue boiling for a suitable period of time. (2 min. for *m*- and *p*-nitroanilines, 10 min. for *o*-nitroaniline.) Add 20 c.c. boiling water and boil until the oil has dissolved. (If solid separates on the addition of water, as will occur with the para compound, gradually add glacial acetic acid with stirring until solution is complete.) Cool, filter off the solid, recrystallise it from dil. acetic acid, dry, and determine the m.p.

*2 : 4-Dinitroaniline* is unchanged by the above treatment owing to its more negative character.

Proceed as indicated under "Acetates" (page 52), and if O.S. does not dissolve readily in the reagent, warm until solution is just complete. Crystallise the acetyl derivative from dilute acetic acid.

**Amides and esters of nitrocarboxylic acids.**

Proceed as indicated under "Amides, anilides, and methyl esters" (page 80) using, of course, ethyl alcohol for an ethyl ester.

***p*-Nitrobenzyl phenyl ether.**

In a 100-c.c. wide-mouthed flask place 1 g. of phenol, ½ g. of solid KOH and 25 c.c. of alcohol. Fit the flask with a reflux condenser, and heat until all the solid has dissolved, then add 1 g. of *p*-nitrobenzyl bromide (or chloride) and boil for 10 min. Add 20 c.c. water, cool and shake. Filter off the solid, wash it with cold water, crystallise from alcohol, dry, and determine the m.p.

***p*-Nitrobenzyl esters of carboxylic acids.**

In a 100-c.c. wide-mouthed flask place ½ g. of the acid and add just sufficient alcohol (or water if the acid is readily soluble) to ssolve it on warming. Add a drop of phenolphthalein soln., then ld 20% aq. KOH, drop by drop, until a permanent red colour is ıst obtained. Add just sufficient of the carboxylic acid to remove ne red colour. Evaporate to dryness on a water bath, and to he residue add ½ g. *p*-nitrobenzyl bromide (or chloride), 2½ c.c. ater and 5 c.c. alcohol. Fit the flask with a reflux condenser, eat the contents to boiling, and continue boiling for ½ hr. (If umping is caused by the separation of solid, add more alcohol.) ool, and if necessary add water to precipitate the ester. Filter ff the solid, wash it well with cold water, crystallise from alcohol, lry, and determine the m.p.

**Preparation of a benzoyl derivative of a primary amine formed by reduction of a nitro compound.**

In a 100-c.c. flask dissolve (if necessary by warming) 1 c.c. or 1 g. of O.S. in 20 c.c. alcohol. Pour in 5 c.c. conc. HCl, then add small quantities of zinc dust, shaking round after each addition, until the liquid is practically colourless. Allow the mixture to settle, then decant off the liquid into a 250-c.c. separating funnel. Cool, pour in 2 c.c. of benzoyl chloride and then add 50 c.c. aq. NaOH. Cool, and shake vigorously for 10 min. Extract the benzoyl derivative with about 30 c.c. ether (see page 21). Wash the ethereal soln., first with dil. HCl, and then with water. Distil off the ether, crystallise the residue from alcohol, dry, and determine the m.p.

## ADDITIONAL NITRO-COMPOUNDS

*Suggestions for the identification of O.S.*

(1) For the identification of alkyl esters of nitrocarboxylic acids proceed as indicated under *A* (page 107). The m.p. of the corresponding acid is given under the name of the ester.

(2) To distinguish between mono-, di-, and trinitro compounds dissolve R.G. of O.S. in 2 c.c. cold acetone and add one drop aq. NaOH. A blue colour indicates a dinitro compound, and a red colour indicates a trinitro compound; mononitro compounds do not give a colour. (R. W. Bost and F. Nicholson, *Ind. Eng. Chem. Anal.*, 1935, 7, 190.)

(3) For reactions and derivatives of the compounds consult the various works of reference.

**Halogen absent.**

***Liquids.***

| B.p. | |
|---|---|
| 265° | *o*-Nitroanisole, $NO_2{\cdot}C_6H_4{\cdot}OMe$. |
| 267° | *o*-Nitrophenetole, $NO_2{\cdot}C_6H_4{\cdot}OEt$. |

***Solids.***

| M.p. | |
|---|---|
| 27° | *m*-Nitrobenzyl alcohol. $NO_2\cdot C_6H_4\cdot CH_2OH$.<br>(*m*-Nitrobenzoic acid, m.p. 141°.) |
| 42° | Ethyl *o*-nitrocinnamate. $NO_2\cdot C_6H_4\cdot CH : CH,COOEt$.<br>(*o*-Nitrocinnamic acid, m.p. 237°.) |
| 54° | *p*-Nitroanisole. $NO_2\cdot C_6H_4\cdot OMe$. |
| 57° | Ethyl *p*-Nitrobenzoate. $NO_2\cdot C_6H_4\cdot COOEt$.<br>(*p*-Nitrobenzoic acid, m.p. 238°.) |
| 59° | *p*-Nitrophenetole. $NO_2\cdot C_6\cdot H_4\cdot OEt$. |
| 68° | 2 : 4 : 6-Trinitroanisole. $(NO_2)_3\cdot C_6H_2\cdot OMe$. |
| 72° | Methyl *o*-nitrocinnamate. $NO_2\cdot C_6H_4\cdot CH : CH\cdot COOMe$<br>(*o*-Nitrocinnamic acid, m.p. 237°.) |
| 74° | *o*-Nitrobenzyl alcohol. $NO_2\cdot C_6H_4\cdot CH_2OH$.<br>(*o*-Nitrobenzoic acid, m.p. 147°.) |
| 78° | 2 : 4 : 6-Trinitrophenetole. $(NO_2)_3\cdot C_6H_2\cdot OEt$. |
| 79° | Methyl *m*-nitrobenzoate. $NO_2\cdot C_6H_4\cdot COOMe$.<br>(*m*-Nitrobenzoic acid, m.p. 141°.) |
| 86° | 2 : 4-Dinitrophenetole. $(NO_2)_2\cdot C_6H_3\cdot OEt$. |
| 88° | 2 : 4-Dinitroanisole. $(NO_2)_2\cdot C_6H_3\cdot OMe$. |
| 93° | *p*-Nitrobenzyl alcohol. $NO_2\cdot C_6H_4\cdot CH_2OH$.<br>(*p*-Nitrobenzoic acid, m.p. 238°.) |
| 94° | *o*-Nitrobenzanilide. Yellow. $NO_2\cdot C_6H_4\cdot NHBz$. |
| 96° | Methyl *p*-nitrobenzoate. $NO_2\cdot C_6H_4\cdot COOMe$.<br>(*p*-Nitrobenzoic acid, m.p. 238°.) |
| 121° | 2 : 4-Dinitroacetanilide. $(NO_2)_2\cdot C_6H_3\cdot NHAc$. |
| 138° | Ethyl *p*-nitrocinnamate. $NO_2\cdot C_6H_4\cdot CH : CH\cdot COOEt$.<br>(*p*-Nitrocinnamic acid, m.p. 285°.) |
| 142° | *m*-Nitrobenzamide. $NO_2\cdot C_6H_4\cdot CONH_2$.<br>(*m*-Nitrobenzoic acid, m.p. 141°.) |
| 152° | *p*-Nitrophenylacetic acid. $NO_2\cdot C_6H_4\cdot CH_2\cdot COOH$. |
| 155° | *m*-Nitrobenzanilide. $NO_2\cdot C_6H_4\cdot NH\cdot Bz$. |
| 161° | Methyl *p*-nitrocinnamate. $NO_2\cdot C_6H_4\cdot CH : CH\cdot COOMe$.<br>(*p*-Nitrocinnamic acid, m.p. 285°.) |
| 168° | Picramic acid. Brownish red. $(NO_2)_2C_6H_2(OH)\cdot NH_2$.<br>(4 : 6 : 1 : 2) |
| 172° | *p*-Dinitrobenzene. $(NO_2)_2\cdot C_6H_4$. |
| 173° | 3 : 5-Dinitrosalicylic acid. $(NO_2)_2C_6H_2(OH)\cdot COOH$.<br>(3 : 5 : 2 : 1) |
| 174° | *o*-Nitrobenzamide. $NO_2\cdot C_6H_4\cdot CONH_2$.<br>(*o*-Nitrobenzoic acid, m.p. 147°.) |
| 182° | 2 : 4-Dinitrobenzoic acid. $(NO_2)_2C_6H_3\cdot COOH$. |
| 188° | Picramide. Yellow. $(NO_2)_3C_6H_2\cdot NH_2$ (2 : 4 : 6 : 1). |
| 199° | *p*-Nitrobenzanilide. $NO_2\cdot C_6H_4\cdot NH\cdot Bz$. |

| M.p. | |
|---|---|
| 201° | *p*-Nitrobenzamide. $NO_2\cdot C_6H_4\cdot CONH_2$.<br>(*p*-Nitrobenzoic acid, m.p. 238°.) |
| 218° | 3-Nitrophthalic acid. $NO_2\cdot C_6H_3(COOH)_2$ (3 : 1 : 2). |
| 230° | 5-Nitrosalicylic acid. $NO_2\cdot C_6H_3(OH)\cdot COOH$ (5 : 2 : 1). |
| 237° | *o*-Nitrocinnamic acid. $NO_2\cdot C_6H_4\cdot CH : CH\cdot COOH$. |
| 285° | *p*-Nitrocinnamic acid. $NO_2\cdot C_6H_4\cdot CH : CH\cdot COOH$. |

**Chlorine present.**

| M.p. | |
|---|---|
| 45° | *m*-Nitrobenzyl chloride. $NO_2\cdot C_6H_4\cdot CH_2Cl$.<br>Oxidation→*m*-nitrobenzoic acid, m.p. 141°. |
| 48° | *o*-Nitrobenzyl chloride. $NO_2\cdot C_6H_4\cdot CH_2\cdot Cl$.<br>Oxidation→*o*-nitrobenzoic acid, m.p. 147°. |
| 54° | Nitro-*p*-dichlorobenzene. $NO_2\cdot C_6H_3Cl_2$ (2 : 1 : 4). |
| 83° | Picryl chloride. Yellow. $(NO_2)_3C_6H_2\cdot Cl$ (2 : 4 : 6 : 1). |

# *DERIVATIVES OF ALDEHYDES AND KETONES*

## A. Compounds of aliphatic aldehydes with ammonia, and with aromatic primary amines.

Hexamine (Hexamethylenetetramine). $(CH_2)_6N_4$.

(*a*) To the soln., obtained in Test 2 (page 167) by boiling O.S. with dil. $H_2SO_4$, add aq. NaOH until alkaline. Warm, and hold a strip of moistened red litmus paper in the mouth of the tube, taking care not to touch the glass,

—paper turned definitely blue, owing to the evolution of $NH_3$.

(*b*) Dissolve R.G. of O.S. in 2 c.c. cold water and add aq. $HgCl_2$, drop by drop,

—white ppt., redissolving on shaking; permanent ppt. after the addition of 4 drops of aq. $HgCl_2$.

(*c*) To 2 c.c. dil. $H_2SO_4$ in a t.t. add 2 R.G. of O.S., heat just to boiling, cool, and apply the following test for formaldehyde.

Add R.G. of resorcinol, then pour 2 c.c. conc. $H_2SO_4$ (from another t.t.) carefully down the side of the tube, —red ring at the junction of the liquids; white ppt., which changes to violet red, forms in the aq. soln.

Methyleneaniline. (Anhydroformaldehydeaniline), $C_6H_5N : CH_2$, m.p. 143°.

Cool the soln. obtained in Test 2 (page 167) by boiling O.S. with dil. $H_2SO_4$ and dilute with water to 5 c.c. Add 5 c.c. of $2\frac{1}{2}$% aq. $NaNO_2$ and filter off the salmon-coloured ppt. formed. Add 2 c.c. of the filtrate to alkaline $\beta$-naphthol ($\frac{1}{8}$-in. layer of $\beta$-naphthol in a t.t. dissolved in 5 c.c. aq. NaOH), —red ppt.

Acetaldehyde ammonia. $CH_3{\cdot}CH(OH){\cdot}NH_2$.

To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. dil. $H_2SO_4$, heat just to boiling, cool, and apply the following test for acetaldehyde :—

Add 3 c.c. of $\frac{1}{2}$% aq. sodium nitroprusside, then add 3 c.c. aq. NaOH,

—wine-red colour, quickly changing to yellow.

### B. Derivatives of benzaldehyde.

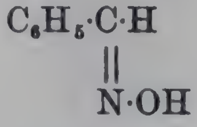
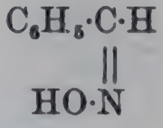
(*a*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. dil. $H_2SO_4$, heat to boiling and continue boiling for 15 sec. Dilute with water to 5 c.c., cool and filter. To the filtrate add an equal volume of $2\frac{1}{2}\%$ aq. $NaNO_2$. Add 2 c.c. of this mixture to alkaline $\beta$-naphthol ($\frac{1}{8}$-in. layer of $\beta$-naphthol in a t.t. dissolved in 5 c.c. aq. NaOH). If no red ppt. is obtained apply Test (*b*).

An immediate, red ppt. indicates that O.S. is a benzal derivative of an aromatic primary amine ($-NH_2$ in nucleus), e.g. benzalaniline. $C_6H_5\cdot N:CH\cdot C_6H_5$, m.p. 54°.

*To identify the amine*, pour 10 c.c. dil. HCl into a 100-c.c. beaker and heat to boiling. Add 2 g. of O.S. and continue boiling with stirring for 1 min., then cool and filter. Add to the filtrate 10 c.c. of 20% aq. KOH, proceeding as described under "Salts of aromatic primary monamines" (page 198).

(*b*) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. dil. $H_2SO_4$, heat to boiling and continue boiling with shaking for $\frac{1}{2}$ min. Cool, dilute with water to 5 c.c. and filter. Add to the filtrate aq. NaOH until it is just alkaline, heat to boiling and add 1 c.c. Fehling's soln. (equal volumes of No. 1 and No. 2).

Immediate reduction (i.e., blue colour disappears and orange ppt. formed) indicates that O.S. is one of the following :—

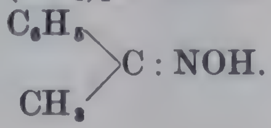
| | | M.p. |
|---|---|---|
| $\alpha$-Benzaldoxime |  $\begin{array}{c} C_6H_5\cdot C\cdot H \\ \| \\ N\cdot OH \end{array}$ | 33° |
| $\beta$-Benzaldoxime |  $\begin{array}{c} C_6H_5\cdot C\cdot H \\ \| \\ HO\cdot N \end{array}$ | 128° |
| Benzaldehyde semicarbazone<br>$C_6H_5\cdot CH:N\cdot NH\cdot CO\cdot NH_2$. | | 214° |

### C. Oximes and semicarbazones.

(These compounds will have been detected by Test 8*A* (page 170).

*Procedure for the identification of O.S.* :—

Determine the m.p. and refer to the following list of m.p.s of oximes and semicarbazones. If one of these m.p.s is identical with, or near to, that of O.S., confirm the identity of O.S. by following the given instructions.

| M.p. | | |
|---|---|---|
| 59° | Acetoxime. | $(CH_3)_2C:NOH$. |
| | Acetophenoxime. |  $\begin{matrix} C_6H_5 \\ CH_3 \end{matrix}\!\!>C:NOH$. |

To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. dil. $H_2SO_4$, heat to boiling and continue boiling for 15 sec. If a clear soln. is obtained proceed as indicated under (*a*); if, however, an emulsion is formed, or oily drops are obtained, proceed as indicated under (*b*).

(*a*) In a 100-c.c. wide-mouthed flask place $\frac{1}{2}$ g. of O.S., 20 c.c. dil. $H_2SO_4$ and some porous pot. Connect the flask to a condenser and distil until 6–7 c.c. is present in the receiver. Apply the following tests for acetone.

(i) To 2 c.c. of the distillate add 2 c.c. of $\frac{1}{2}$% aq. sodium nitroprusside, then add 2 drops aq. NaOH,
—wine-red colour, changed to violet red by acetic acid.

(ii) Add one drop of the distillate to 2 c.c. iodine soln., then add aq. NaOH, drop by drop, until the deep brown colour disappears,
—pale yellow ppt. of iodoform, with characteristic odour.

(iii) From the remainder of the distillate prepare a 2 : 4-dinitrophenylhydrazone in the manner described on page 66. (Acetone 2 : 4-dinitrophenylhydrazone, m.p. 126°.)

(*b*) In a 100-c.c. wide-mouthed flask place 1 g. of O.S., 5 c.c. conc. HCl, 5 c.c. water and some porous pot. Heat to boiling under a reflux condenser and continue boiling for 10 min. Cool, and transfer the contents of the flask to a small separating funnel. Extract with ether (see page 21), wash the ethereal soln. twice with about 3 c.c. water, then distil off the ether.

(i) Apply the following test for acetophenone :—Dip the end of a glass rod into the residue, then immerse the end of the rod in 2 c.c. of $\frac{1}{2}$% aq. sodium nitroprusside and stir for 15 sec. To the soln. add 2 drops aq. NaOH,

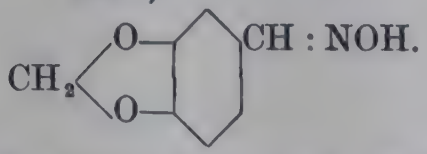
M.p.

—wine red colour, turned blue by acetic acid.

(ii) From the residue prepare a phenylhydrazone in the manner described on page 65.

(Acetophenone phenylhydrazone turns brown and shrinks at 100°, and is completely melted at 102°–103°.)

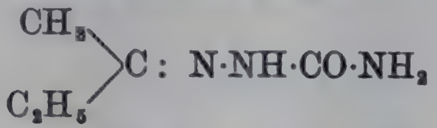
110° Piperonaldoxime.



Hydrolyse O.S. by the method indicated under "M.p. 59° (*b*)." From the residue obtained after distilling off the ether prepare a phenylhydrazone in the manner described on page 66.

(Piperonal phenylhydrazone, m.p. 100°.)

148° Methyl ethyl ketone semicarbazone.



$$\begin{matrix} CH_3 \\ C_2H_5 \end{matrix} \Big> C : N{\cdot}NH{\cdot}CO{\cdot}NH_2$$

Proceed as indicated under "M.p. 59° (*a*)" when similar results will be obtained, except that in Test (i) the wine red colour is little affected by acetic acid.

(2 : 4–Dinitrophenylhydrazone of methyl ethyl ketone, m.p. 111°.)

141° Benzophenoxime. $(C_6H_5)_2C : NOH$.

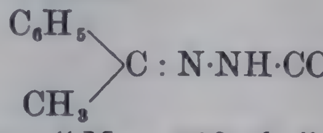
Hydrolyse O.S. by the method indicated under "M.p. 59° (*b*)." From the residue obtained after distilling off the ether prepare a phenylhydrazone in the manner described on page 66.

(Benzophenone phenylhydrazone, m.p. 137°.)

187° Acetone semicarbazone. $(CH_3)_2C : N{\cdot}NH{\cdot}CO{\cdot}NH_2$.

Proceed as indicated under "M.p. 59° (*a*)," when similar results will be obtained.

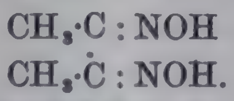
198° Acetophenone semicarbazone.



$$\begin{matrix} C_6H_5 \\ CH_3 \end{matrix} \Big> C : N{\cdot}NH{\cdot}CO{\cdot}NH_2.$$

Proceed as indicated under "M.p. 59° (*b*)," when similar results will be obtained.

234° Dimethylglyoxime.



$$\begin{matrix} CH_3{\cdot}C : NOH \\ | \\ CH_3{\cdot}C : NOH. \end{matrix}$$

(*a*) Dissolve R.G. of O.S. in 2 c.c. alcohol and add one drop dil. $NH_4OH$. Add to nickel sulphate soln. (R.G. of solid dissolved in 2 c.c. water.) —red ppt. of nickel dimethylglyoxime.

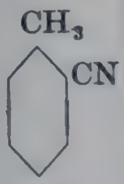
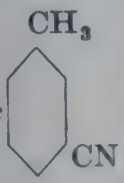
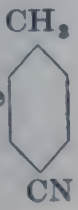
(*b*) *Preparation of diacetyl derivative*, m.p. 115°.

In a dry t.t. place ½ g. of O.S. and add 2 c.c. acetic anhydride. Heat until solution is just complete. Cool, add 10 c.c. water and shake. Filter, crystallise the solid from water, dry, and determine the m.p.

## *NITRILES*

The identity *of* O.S. is indicated by the carboxylic acid produced by hydrolysis (Test 9 *B*, page 171). See list of carboxylic acids below. The reduction test (described on page 241) is a confirmatory general test for nitriles.

Confirm the identity of O.S. by preparing and determining the m.p. of the corresponding amide (for method of preparation see page 241); or by determining the b.p. of O.S. (acetamide and propionamide are deliquescent solids).

| *Acid detected* | *M.p. of acid* | *Nitrile indicated* | | *B.p.* | *M.p. of amide* |
|---|---|---|---|---|---|
| Acetic | — | Acetonitrile<br>$CH_3{\cdot}CN$ | Miscible with water. Pleasant odour | 81° | — |
| Propionic | — | Propionitrile<br>$CH_3{\cdot}CH_2{\cdot}CN$ | | 98° | — |
| Phenylacetic | 76° | Phenylacetonitrile<br>$C_6H_5{\cdot}CH_2{\cdot}CN$ | Insoluble in water. Odour resembling that of bitter almonds | 231° | 157° |
| *o*-Toluic | 102° | *o*-Tolunitrile  | | 204° | 141° |
| *m*-Toluic | 110° | *m*-Tolunitrile  | | 210° | 94° |
| Benzoic | 121° | Benzonitrile<br>$C_6H_5{\cdot}CN$ | | 190° | 128° |
| *p*-Toluic | 178° | *p*-Tolunitrile  | | *M.p.*<br>29° | 158° |

*Reduction test for nitriles.*

To 5 c.c. alcohol in a t.t. add one drop of O.S. and a piece of clean sodium (roughly ¼-in. cube). When all the metal has disappeared add one or two drops of chloroform and heat to boiling in a fume cupboard, —obnoxious carbylamine odour, indicating that a primary amine has been formed. Immediately the odour is detected, cool, and add excess of conc. HCl in order to destroy the isocyanide.

*Preparation of an amide from a nitrile.*

Into a 100-c.c. conical flask pour 10 c.c. $H_2O_2$ (15–20 volume) and 2 c.c. aq. NaOH. Add ½ c.c. of O.S. (or ½ g. if solid) and stand the flask in water which has been heated to about 40°. (Do not cork the flask as oxygen will be evolved.) Periodically remove the flask and shake vigorously until all the oil has disappeared, and only a white solid is present. Filter off the solid, wash it with cold water, crystallise from water, dry, and determine the m.p.

(Benzonitrile and phenylacetonitrile are converted to the amides in about 10 min.; the tolunitriles require from one to several hours.)

## *ALKYL NITRITES AND NITRATES*

Apply both the following tests to O.S.

(*a*) Into a dry t.t. pour one drop of O.S. and add one drop of conc. $H_2SO_4$. The immediate evolution of red fumes indicates that O.S. is a nitrite. (The liquid also becomes red-brown in colour.) With alkyl nitrates no red fumes are evolved and the liquid remains colourless.

(*b*) To 5 c.c. of a cold mixture of equal volumes of water and conc. $H_2SO_4$ add a trace of diphenylamine, shake for ½ min. (see note 1), then add one drop of O.S. An immediate, *deep* blue colour indicates that O.S. is a nitrite.

Determine the b.p. of O.S. and refer to the following list of b.p.s of alkyl nitrites (see note 3).

If a deep blue colour is not immediately obtained, or only a pale blue colour is produced (see note 2), stand the t.t. in boiling water for 1 min., then remove and shake. A *deep* blue colour indicates that O.S. is a nitrate. Determine the b.p. of O.S. and refer to the following list of b.p.s of alkyl nitrates (see note 3).

NOTES.

(1) A pale blue colour may be obtained when the diphenylamine is added to the acid, owing to the presence in the

latter of traces of $HNO_2$; this pale tint, however, will not interfere with the test which requires, for a positive result, a very deep blue colour.

(2) Some alkyl nitrates (e.g. ethyl nitrate) give a pale blue colour in the cold, changing to a deep blue on standing for 2 min.; others, (e.g. amyl nitrate) only yield a blue colour on heating.

(3) For further confirmation of identity the equiv. wt. of the ester may be determined by the method described on page 112.

**Alkyl nitrites.**

| B.p. | |
|---|---|
| 75° | *n*-Butyl nitrite. $C_4H_9{\cdot}O{\cdot}N:O$. Penetrating odour. |
| 96° | *iso*-Amyl nitrite. $C_5H_{11}{\cdot}O{\cdot}N:O$. Pale yellow. Penetrating odour. The inhalation of the vapour dilates the blood vessels and causes the face to flush, at the same time producing giddiness. |

**Alkyl nitrates.**

| B.p. | |
|---|---|
| 86° | Ethyl nitrate. $C_2H_5{\cdot}O{\cdot}NO_2$. Pleasant odour. |
| 147° | *iso*-Amyl nitrate. $C_5H_{11}{\cdot}O{\cdot}NO_2$. Penetrating odour. |

## *PURINE GROUP*

*Procedure:—*

To the residue obtained in Test 6 (page 170), add 2–3 drops aq. NaOH. If the violet-red colour is immediately destroyed proceed as indicated under "Caffeine, etc.," otherwise as under "Uric acid, etc."

**Caffeine (or its salts), theophylline.**

If the aq. soln. of O.S. is

(*a*) neutral, dissolve R.G. of O.S. in 2 c.c. water. To the cold soln. add 1 c.c. aq. mercurous nitrate.

A white ppt. indicates that O.S. is theophylline, m.p. 264°. *If no ppt. is obtained*, to ⅛-in. layer of O.S. in a t.t. add 2 c.c. water, heat until solution is complete, then cool. Add 1 c.c. aq. $HgCl_2$ and shake.

A white crystalline ppt. (formed in a few seconds) indicates that O.S. is caffeine, m.p. 234°.

(*b*) definitely acid, a salt of caffeine is indicated. (As caffeine is a weak base the salts are hydrolysed by water.)

(i) Dissolve R.G. of O.S. in 5 c.c. water. To the cold soln. add one drop aq. $FeCl_3$.

A violet colour indicates that O.S. is caffeine salicylate. Isolate salicylic acid in the manner described under (iii) and determine its m.p. (158°).

If no violet colour is obtained apply Test (ii).

(ii) Dissolve R.G. of O.S. in 2 c.c. water, add 1 c.c. Denigès soln., heat to boiling and add one drop aq. $KMnO_4$. Disappearance of the purple colour, *and a white ppt.* indicates that O.S. is caffeine citrate.

If a negative result is obtained apply Test (iii).

(iii) To ½-in. layer of O.S. in a t.t. add 5 c.c. water, heat until solution is complete, then cool well and shake. If a ppt. is obtained, filter, wash the solid with cold water, dry, and determine the m.p.

M.p. 121° indicates that the ppt. is benzoic acid and therefore O.S. is caffeine benzoate.

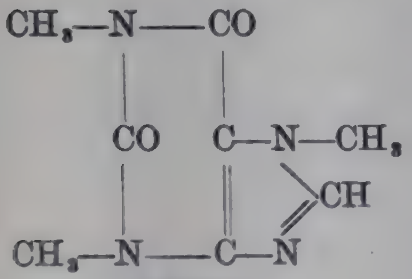
**Uric acid, theobromine.**

Dissolved R.G. of O.S. in 2 c.c. aq. $Na_2CO_3$. To the cold soln. add 1 c.c. aq. $AgNO_3$ and shake.

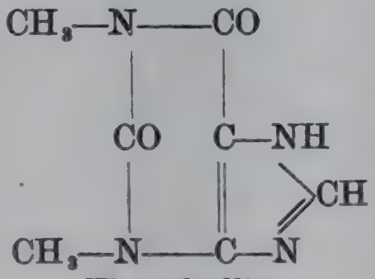
A dark grey or black ppt. indicates that O.S. is uric acid. (Only very slightly soluble in boiling water; aq. soln. slightly acid.)

A white ppt. indicates that O.S. is theobromine. (Only slightly soluble in boiling water; aq. soln. neutral to litmus. Amphoteric, ⅛-in. layer in a t.t. will dissolve in 2 c.c. cold aq. NaOH, or in 5 c.c. boiling dil. HCl.)

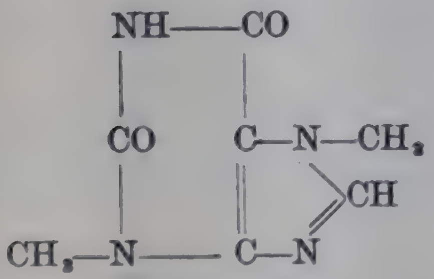
*Formulæ of members of the purine group*



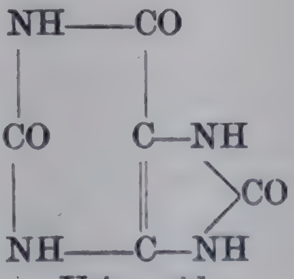
Caffeine.



Theophylline.



Theobromine.



Uric acid.

## *ALKALOIDS*

(Except in the case of the commoner alkaloids or their salts the student will probably have been informed that the compound given for identification is an alkaloidal substance.)

Some alkaloids will commonly be encountered either as the free base or as a salt, others only as salts.

The free alkaloids are insoluble or only sparingly soluble in water, whereas the salts are usually soluble and yield a ppt. of the free alkaloid on the addition to their aq. soln. of aq. NaOH or aq. $Na_2CO_3$. (Morphine, owing to its phenolic character, dissolves readily in excess of aq. NaOH but not in excess of aq. $Na_2CO_3$.)

Quinidine, cinchonine, cinchonidine, brucine and cocaine will usually be met with either as the free base, or as the hydrochloride or sulphate; diamorphine and apomorphine usually only as the hydrochloride.

In addition to the free base, hydrochloride, or sulphate, morphine may be present as tartrate; atropine as salicylate; and strychnine as nitrate, phosphate, or acetate.

Codeine will usually be present as free base or phosphate; and quinine as free base, sulphate, or hydrochloride, and is also met with as hydrobromide, hydriodide, phosphate, hypophosphite, arsenate, formate, acetate, lactate, citrate, and salicylate.

NOTES CONCERNING THE TESTS.

(1) By a trace is indicated an amount of substance roughly equal in bulk to an ordinary pin-head.

(2) To moisten a substance with a reagent, dip the rounded end of a glass rod into the specified reagent to the depth of about ¼ in., withdraw it from the liquid and remove the excess of the reagent by touching the end of the glass rod against the inside of the neck of the bottle; then stir the substance, in a porcelain dish, with the moistened end of the glass rod.

### General tests for alkaloids and their salts.

If O.S. is an alkaloid or one of its salts a positive result will have been obtained in Test 1 (below). See note (page 245).

To confirm that O.S. is an alkaloidal substance apply Test 2, when a positive result should be obtained.

Alkaloids will also give the reactions under Tests 3 and 4.

For any one of the following tests dissolve R.G. of free alkaloid or salt in 2 c.c. dil. HCl, then add the stated number of drops of the appropriate reagent.

(1) 2 drops Mayer's reagent.
—white or pale yellow ppt.
(Mayer's reagent :—13·5 g. $HgCl_2$, 50 g. KI, 940 c.c. water.)

(2) 1 drop Dragendorff's (Thresh's) reagent.
—orange red ppt.
(Thresh's reagent :—Dissolve 8 g. $Bi(NO_3)_3$ in 20 c.c. $HNO_3$ (1 pt. conc. $HNO_3$, 2 pts. water); also dissolve 27 g. KI in 40 c.c. water. Mix the solutions with constant stirring and allow to stand. Pour off from the crystals of $KNO_3$ which separate, and make up to 100 c.c. with distilled water.)

(3) 1 drop of a soln. of iodine in KI,
—brown ppt.

(4) 10 drops of saturated aq. picric acid,
—yellow ppt.

NOTE.

Salts of pyridine and of quinoline give a ppt. with Mayer's reagent. If on treatment of O.S. with aq. NaOH (Test 1, page 166) oily drops were obtained, isolate the base in the manner described under "Salts of aromatic primary monamines" (page 198), then proceed as indicated under "Quinoline," (*c*) and (*d*) page 215. If with the aq. NaOH no oily drops were obtained, but a pungent, peculiar odour was produced, see under "Pyridine" (page 214).

SCHEME FOR THE DETECTION OF THE FOLLOWING ALKALOIDS OR THEIR SALTS :—Quinine, quinidine, cinchonine, cinchonidine, morphine, codeine, apomorphine, diamorphine (heroin), strychnine, brucine, atropine, cocaine.

*A*. Place R.G. of O.S. in a t.t., add 2 drops dil. $H_2SO_4$, dilute with water to 10 c.c. and look through the depth of the liquid over a dark surface.

If a blue fluorescence is observed apply to the soln. the tests for quinine and quinidine (page 246); if negative results are obtained apply Test (*c*) under *B* for cinchonidine, since this alkaloid yields a slight blue fluorescence.

If there is no blue fluorescence apply Test B.

*B*. Moisten a trace of O.S. with conc. $HNO_3$.

*Colour produced.*

—purple red, changing to red-brown indicates that O.S. is apomorphine or one of its salts. Apply the confirmatory tests (page 247).

—immediate blood-red, indicates that O.S. is brucine (m.p. 178°) or one of its salts. Confirm as follows :—Evaporate the red liquid to dryness on a water bath. Add a drop of $SnCl_2$ soln. and stir,—violet colour. (The $SnCl_2$ soln. may be prepared by dissolving $\frac{1}{8}$-in. layer of solid $SnCl_2$ in a t.t. in 2 c.c. hot conc. HCl, then cooling and diluting with 2 c.c. water.)

*Colour produced.*

—orange-red, almost immediate, indicates that O.S. is morphine or one of its salts. Proceed as described for brucine (immediately above),—yellow residue, giving no violet colour with $SnCl_2$ soln. Apply the confirmatory tests on page 247.

—deep yellow, rapidly becoming lighter, indicates that O.S. is codeine or one of its salts. Apply the tests on page 247.

—yellow. Moisten R.G. of O.S. with conc. $HNO_3$ and heat on a water bath. Blue-green colour, which disappears on further heating, indicates that O.S. is diamorphine (m.p. 171°) or one of its salts. Apply the confirmatory tests on page 247.

*No colour produced.*

(*a*) To the mixture add a trace of powdered $KClO_3$ and stir. A red colour indicates that O.S. is strychnine or one of its salts. Apply the confirmatory tests on page 248.

If no red colour is produced apply Test (*b*).

(*b*) Moisten a trace of O.S. with conc. $HNO_3$, evaporate to dryness on a water bath and cool. Moisten the residue with freshly prepared alcoholic KOH. If a violet colour is obtained apply the confirmatory test for atropine or one of its salts (page 248).

If no violet colour is obtained apply Test (*c*).

(*c*) Place R.G. of O.S. in a crucible, add two or three drops dil. HCl and evaporate to dryness. Gently heat the residue with a small flame.

If a violet colour is produced with evolution of violet vapours, apply the distinguishing test for cinchonine and cinchonidine or their salts (page 248).

If no violet colour and vapours are obtained apply the test for cocaine (page 248).

## CONFIRMATORY AND DISTINGUISHING TESTS FOR ALKALOIDS AND THEIR SALTS

**Quinine and quinidine.**

To the blue fluorescent soln. add Br water drop by drop until the soln. is *just* tinted yellow. Divide the soln. into two equal portions.

*To one portion* add 1 c.c. dil. $NH_4OH$.

An emerald green colour is given by both quinine and quinidine and their salts.

*To the other portion* add a trace of solid $K_3Fe(CN)_6$, shake and add 1 c.c. dil. $NH_4OH$.

A rose-red colour is given by both quinine and quinidine and their salts.

*Distinguish as follows* :—

To ½-in. layer of Rochelle salt in a t.t. add 1 c.c. water, heat until solution is complete, then cool. Dissolve R.G. of O.S. (see note below) in 1 c.c. water, add the soln. to the aq. Rochelle salt and shake.

A crystalline ppt. indicates that O.S. is quinine or one of its salts.

NOTE.

If O.S. is not soluble in water, place R.G. in a porcelain dish, add two or three drops dil. HCl and evaporate to dryness on a water bath. Dissolve the residue in 1 c.c. water.

**Apomorphine hydrochloride.**

Dissolve R.G. of O.S. in 1 c.c. water and add 2 c.c. of a cold saturated aq. soln. of $NaHCO_3$,

—white ppt. becoming green on standing. Shake, and divide the green mixture into two equal portions. To one portion add 1 c.c. chloroform and to the other portion add 1 c.c. ether; shake the mixtures. The green ppt. dissolves in chloroform yielding a violet-blue soln., and in ether yielding a purple soln.

**Morphine, codeine, and diamorphine (heroin).**

(*a*) Moisten a trace of O.S. with formalin, then add 5 drops conc. $H_2SO_4$ and stir.

A violet-red colour, changing to violet-blue, is given by morphine and diamorphine, whereas codeine immediately gives a violet-blue colour. Apply Test (*b*).

(*b*) Moisten a trace of O.S. with Froede's reagent (1 g. $NH_4$ molybdate dissolved in 100 c.c. conc. $H_2SO_4$).

An immediate violet colour indicates that O.S. is morphine or diamorphine. To distinguish apply Tests (*c*) and (*d*).

An immediate green colour indicates that O.S. is codeine, m.p. 155°.

(*c*) Add R.G. of O.S. to 2 c.c. of 1% $KIO_3$ soln., then add 1 drop dil. $H_2SO_4$ and allow to stand for 1 min.

If a yellow-brown colour is obtained, add 1 c.c. chloroform and shake. A violet lower layer (due to a soln. of liberated iodine in the chloroform) indicates that O.S. is morphine. (Diamorphine and codeine do not liberate iodine from acidified $KIO_3$.)

(*d*) If O.S. is

(i) a salt, dissolve R.G. in 1 c.c. water.

(ii) a free alkaloid, place R.G. in a porcelain dish, add two or three drops dil. HCl and evaporate to dryness on a water bath. Dissolve the residue in 1 c.c. water.

To the soln. obtained add one drop aq. $FeCl_3$.

A deep blue colour (due to a phenolic group) indicates that O.S. is morphine. (No colour is obtained with diamorphine or codeine.)

**Strychnine.**

(*a*) Moisten a trace of O.S. with Mandelin's reagent (1 g. $NH_4$ vanadate dissolved in 100 c.c. conc. $H_2SO_4$),
—deep blue colour changing to violet, then to red. (The change to red takes place more quickly on warming.)

(*b*) Moisten a trace of O.S. with conc. $H_2SO_4$, add a trace of $MnO_2$ and stir,
—deep violet colour changing to red.

**Atropine,** m.p. 115°.

Stir R.G. of O.S. with 2 drops conc. $H_2SO_4$ and a trace of solid $NaNO_2$,
—deep yellow colour. Add a drop of alcoholic KOH,—colour changes to violet.

**Cinchonine,** m.p. 255°, **and cinchonidine,** m.p. 210°.

Dissolve R.G. of O.S. in 2 drops dil. HCl, add 1 c.c. $K_4Fe(CN)_6$ soln.,
—pale yellow flocculent ppt.

Warm slightly and shake,—ppt. dissolves.

Continue shaking for about ½ min. The separation of golden spangles indicates that O.S. is cinchonine.

**Cocaine,** m.p. 98°.

If O.S. is a salt apply Tests (*a*) and (*b*) ; if a free alkaloid evaporate R.G. with two or three drops of dil. HCl to dryness on a water bath and apply Tests (*a*) and (*b*) to the residue.

(*a*) Dissolve R.G. of O.S. or the residue in 1 c.c. aq. $K_2CrO_4$,
—clear yellow soln. Add one drop conc. HCl,—yellow ppt.

(*b*) Dissolve R.G. of O.S. or the residue in 1 c.c. water, add 1 c.c. aq. $KMnO_4$ and shake,
—purple ppt. (cocaine permanganate).

# SCHEME V

## Compounds containing N and S (not as sulphate)

If O.S. is a liquid see "Isothiocyanates" (page 252); if a solid follow the procedure below.

***O.S. solid.***

If O.S. contains

- (*a*) a metal, proceed as indicated under "Metal present" (page 250).
- (*b*) no metal, follow the procedure below.

**No metal present.**

(1) To ⅛-in. layer of O.S. in a t.t. add 2 c.c. aq. NaOH, gently shake and hold a narrow strip of moistened red litmus paper in the mouth of the tube, taking care not to touch the glass. If the colour of the paper is

- (*a*) changed to a definite blue (indicating that O.S. is an ammonium salt), add R.G. of O.S. to 2 c.c. water in a t.t. and shake until solution is complete. Add 2 c.c. aq. $FeCl_3$, and fill up the t.t. with water.

  A deep red colour indicates that O.S. is a thiocyanate. If a deep red colour is not produced, proceed as indicated under Test 2 in order to ascertain if O.S. is an aminosulphonate, or a nitrosulphonate; if it is neither, proceed as indicated under "Sulphonic acids of hydrocarbons and their salts" (page 158).
- (*b*) unaffected, or little affected, heat the contents of the t.t. to boiling and continue boiling gently for ½ min. Cool, and add one drop aq. lead acetate. If a dark brown or black colour is produced see "Thioureas" (page 253); if no such colour is obtained proceed as follows:—To 2 c.c. water in a t.t. add R.G. of O.S. and heat to boiling with shaking. Test the hot liquid with blue litmus paper; if acid, apply Test 2; if neutral, apply Test 3.

(2) To 5 c.c. of a mixture of equal volumes of dil. HCl and 2½% aq. $NaNO_2$ add R.G. of O.S.; close the mouth of the t.t. and invert several times. Add 2 c.c. of the soln. to alkaline β-naphthol (⅛-in. layer of β-naphthol in a t.t. dissolved in 5 c.c.

aq. NaOH). If a red soln. is produced (due to the formatio of a soluble azo compound) see " Aminosulphonic acids an their salts " (page 251). If any other result is obtained appl Test 8*B* (page 171); if in this test a red soln. is produced wit the alkaline β-naphthol see " Nitrosulphonic acids and thei salts " (page 252); if, however, a red soln. is not obtaine apply Test 3, and then the tests under " Saccharin " (page 256

(3) To ⅛-in. layer of O.S. in a *dry* t.t. add 5 drops conc. $H_2SO_4$ Heat for 10 sec. over a flame (about 1 in. high), cool, and carefully dilute with water to 2 c.c. Add sufficient solid NaO to render the mixture alkaline, and hold a strip of moistene red litmus paper in the mouth of the tube, taking care not t touch the glass.

If the colour of the paper is

(*a*) changed to a definite blue (the odour of $NH_3$ will usually be detected) see " Sulphonamides, and saccharin (page 254).

(*b*) unaffected, or little affected, apply Test 4.

(4) To R.G. of O.S. in a *dry* t.t. add 5 drops conc. $H_2SO_4$. Hea for 10 sec. over a flame (about 1 in. high), cool, and carefull dilute with water to 5 c.c.. Again cool, and add 5 c.c. of 2½% aq. $NaNO_2$. Add 2 c.c. of this mixture to alkaline β-naphtho (⅛-in. layer of β-naphthol in a t.t. dissolved in 5 c.c. aq. NaOH

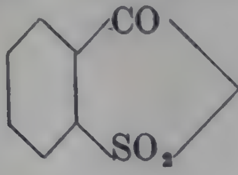
If an intense, red-coloured soln. or ppt. is produced (due t the formation of an azo compound), determine the m.p. o O.S. and refer to the list of m.p.s of sulphonyl derivatives o aromatic primary amines (page 257).

If any other result is obtained, place the equivalent of ⅛-i layer in a t.t. of O.S. in a 100-c.c. wide-mouthed flask an add 2½ c.c. each of water and conc. $H_2SO_4$. Fit the flask wit a reflux condenser, heat the contents to boiling and continu boiling for 15 min. Cool, and dilute with water to 25 c.c If the soln. is not perfectly clear, filter until this condition i attained. Pour into a separating funnel and proceed fro " add 1 c.c. of 2½% aq. $NaNO_2$ " as described under " Nitrosamine test " (page 172).

If a nitrosamine is detected in the Liebermann's reactio determine the m.p. of O.S. and refer to the list of m.p.s o sulphonyl derivatives of secondary amines (page 257).

**Metal present.**

(Only compounds containing an alkali metal are here considered To 2 c.c. water in a t.t. add R.G. of O.S. and shake until solutio is complete. Add 2 c.c. aq. $FeCl_3$, and fill up the t.t. with wate A deep red colour indicates that O.S. is a thiocyanate. If a dee red colour is not produced, proceed as indicated under Test page 249) in order to ascertain if O.S. is an aminosulphonate, a itrosulphonate, or the sodium derivative of saccharin (soluble accharin,



$N{\cdot}Na$, $2H_2O$.)

## AMINOSULPHONIC ACIDS AND THEIR SALTS

(Only sulphanilic, metanilic, and naphthionic acids and their lkali salts are here considered. The free acids decompose on heating.)

*Procedure for the identification of O.S.*:—

Apply the following distinguishing tests. Also apply any tests given under the name of the aminosulphonic acid indicated, and confirm its identity (if a free acid) by a determination of its equiv. wt. by Method 1 (page 81).

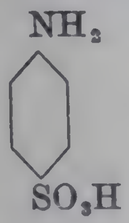
*Distinguishing tests.*

(1) To ⅛-in. layer of O.S. in a t.t. add 2 c.c. aq. $Na_2CO_3$ (or 2 c.c. water if O.S. is an alkali salt), warm until solution is complete, then fill up the t.t. with water.

If a violet fluorescence is observed see "Naphthionic acid"; if there is no fluorescence apply Test 2 in order to distinguish between sulphanilic acid and metanilic acid.

(2) To 2 c.c. water add R.G. of O.S. and heat until solution is complete. To the hot soln. add Br water until, after shaking, the soln. is pale yellow. If a ppt. is obtained see "Sulphanilic acid," or if there is no ppt. see "Metanilic acid."

Sulphanilic acid.



Equiv. wt. (anhydrous) 173·1.

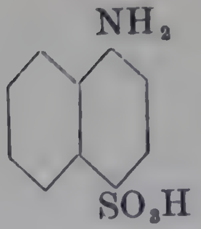
Yields aniline on heating with soda-lime (Test 3, page 6).

(*a*) To ⅛-in. layer of O.S. in a t.t. add 2 c.c. dichromate mixture and heat to boiling,

—pungent odour of *p*-benzoquinone.

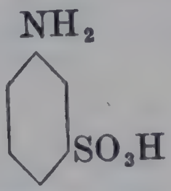
(*b*) *Preparation of 2 : 4 : 6-tribromoaniline*, m.p. 119°.

To a soln. of O.S. in hot water add strong Br soln. (10 c.c. Br, 15 g. KBr, 100 c.c. water) until after stirring the liquid is pale yellow. Filter off the ppt. formed, wash it well with cold water, dry, and determine the m.p.

Naphthionic acid.  Equiv. wt. 223·1.

Yields α-naphthylamine on heating with soda-lime (Test 3, page 6).

To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 2 c.c. dichromate mixture and heat to boiling,
—pungent odour of α-naphthaquinone.

Metanilic acid.  Equiv. wt. 173·1.

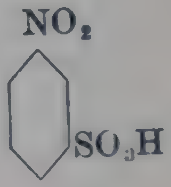
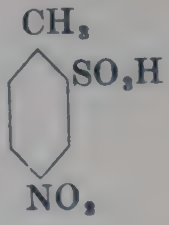
Gives no characteristic odour on heating with soda-lime since *m*-aminophenol is formed.

Yields no quinone on heating with dichromate mixture.

## *NITROSULPHONIC ACIDS AND THEIR SALTS*

*Procedure for the identification of O.S.* :—

Prepare a sulphonamide in the manner described on page 159, (crystallise from alcohol) and determine its m.p., then refer to the following list of m.p.s of sulphonamides.

| *M.p. of sulphonamide.* | *Nitrosulphonic acid indicated.* | |
|---|---|---|
| 162° | *m*-Nitrobenzenesulphonic acid. |  |
| 186° | *p*-Nitrotoluene-2-sulphonic acid. |  |

## *ISOTHIOCYANATES*

These compounds possess a pungent mustard-like odour.

Apply the general tests (*a*) and (*b*), then identify the isothic cyanate by proceeding as indicated under (*c*).

(*a*) To 2 c.c. alcohol add one drop each of aq. $HgCl_2$ and ac NaOH, then add one drop of O.S. and warm,
—black ppt. of HgS.

(*b*) To 5 c.c. alcohol add one drop of O.S., 1 c.c. dil. HCl and the equivalent of $\frac{1}{8}$-in. layer in a t.t. of zinc dust. Shake, more or less continuously, for 5 min.,

—leek-like odour, due to the formation of thioformaldehyde, $CH_2S$.

Filter, and to the filtrate add solid NaOH until alkaline, then add 1–2 drops of chloroform. Heat to boiling in a fume cupboard and continue boiling for 15 sec.,

—obnoxious carbylamine odour, indicating that O.S. has been reduced to a primary amine. Immediately the odour is detected, cool and add excess of conc. HCl in order to destroy the isocyanide.

(*c*) *Preparation of a thiourea.*

To 1 c.c. of O.S. in a porcelain dish add 10 c.c. conc. $NH_4OH$ and evaporate on a water bath. Crystallise the solid from water, dry, and determine the m.p.

| *M.p. of thiourea.* | *Thiourea indicated.* | *Inference that O.S. is* |
|---|---|---|
| 74° | Allylthiourea | Allyl isothiocyanate, b.p. 150°.<br>$CH_2 : CH{\cdot}CH_2{\cdot}N : CS$. |
| 154° | Phenylthiourea | Phenyl isothiocyanate, b.p. 221°.<br>$C_6H_5{\cdot}N : CS$. |

## *THIOUREAS*

Indicated by a brown or black colour obtained after boiling with aq. NaOH and adding aq. lead acetate (Test 1, page 249).

*Procedure for the identification of O.S.* :—

Determine the m.p. and refer to the following list of m.p.s of thioureas. If one of these m.p.s is identical with, or near to, that of O.S., confirm the identity of O.S. by applying the given tests.

M.p.

74° Allylthiourea (Thiosinamine). $CH_2 : CH{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH_2$.

*Preparation of acetyl derivative*, m.p. 98°-100°.

To $\frac{1}{4}$-in. layer of O.S. in a t.t. add 5 c.c. acetone and shake until solution is complete. To the soln. add gradually 2 c.c. acetyl chloride and shake. Filter, wash the solid with acetone, dry, and determine the m.p.

151° Diphenylthiourea (Thiocarbanilide). $C_6H_5{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5$.

Practically insoluble in hot water.

154° Phenylthiourea. $C_6H_5{\cdot}NH{\cdot}CS{\cdot}NH_2$. Soluble in hot water.

(*a*) To R.G. of O.S. in a dry t.t. add 5 drops of conc.

$H_2SO_4$. Heat for 5 sec. over a small flame (about 1 in. high), cool, and carefully dilute with water to 5 c.c. Again cool, and add 5 c.c. of 2½% aq. $NaNO_2$. Add 2 c.c. of this mixture to alkaline β-naphthol (⅛-in. layer of β-naphthol in a t.t. dissolved in 5 c.c. aq. NaOH).

A red solution (due to the formation of an azo compound and indicating that the sulphate of a primary aromatic amine has been formed by the treatment of O.S. with conc. $H_2SO_4$) is obtained with both compounds. Apply Test (*b*).

(*b*) To ⅛-in. layer of O.S. in a dry t.t. add 5 drops conc. $H_2SO_4$. Heat for 5 sec. over a small flame (about 1 in. high), cool, and carefully dilute with water to 2 c.c.. Add sufficient solid NaOH to render the mixture alkaline, and hold a strip of moistened red litmus paper in the mouth of the tube, taking care not to touch the glass.

If the colour of the paper is changed to a definite blue (due to the evolution of $NH_3$) this indicates that O.S. is phenylthiourea. With diphenylthiourea the colour of the paper will be unaffected, or only very slightly affected.

172° –180° Thiourea. $NH_2{\cdot}CS{\cdot}NH_2$.

(*a*) Heat R.G. of O.S. in a dry t.t. over a small flame until the solid melts and continue heating for 5 sec. Apply the following test for $NH_4$ thiocyanate. Add 2 c.c. water, shake until the solid has dissolved, then add 2 c.c. aq. $FeCl_3$. Nearly fill the t.t. with water, close the mouth and invert, —deep red soln.

(*b*) To 2 c.c. of dil. acetic acid add 2 R.G. of O.S. and heat until solution is complete. To the hot soln. add 2 c.c. aq. $K_4Fe(CN)_6$, —green colour, changing to blue.

## *SULPHONAMIDES AND SACCHARIN*

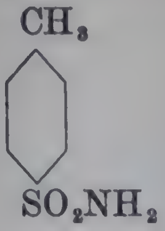
These compounds will have been indicated by the evolution of $NH_3$ in Test 3 (page 250).

*Procedure for the identification of O.S.*:—

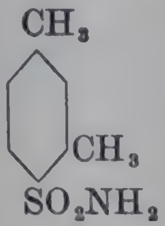
Determine the m.p. and refer to the following list of m.p.s. If one of these m.p.s is identical with, or near to, that of O.S., confirm the identity of O.S. by following the given procedure.

M.p. 137°

*p*-Toluenesulphonamide.



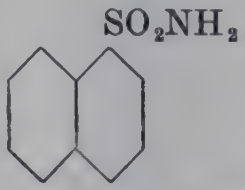
*m*-Xylene-4-sulphonamide.



Proceed as indicated under " Preparation of dimethyl derivatives " (page 257). The formation of a solid derivative, m.p. 80°, indicates that O.S. is *p*-toluenesulphonamide.

With *m*-xylene-4-sulphonamide the oil obtained does not solidify.

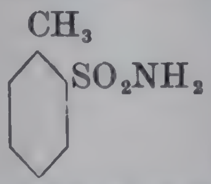
150° Naphthalene-1-sulphonamide.



In a 100-c.c. wide-mouthed flask place the equivalent of $\frac{1}{4}$-in. layer in a t.t. of O.S. and add 5 c.c. each of water and conc. $H_2SO_4$. Fit the flask with a reflux condenser, heat the contents to boiling and continue boiling for 5 min. A deposit of naphthalene (characteristic odour) will be present in the condenser tube. Wash out the deposit with water, filter it off, dry, and determine the m.p. (M.p. of naphthalene, 80°.)

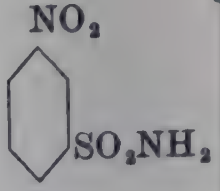
153° Benzenesulphonamide. $C_6H_5{\cdot}SO_2NH_2$

154° *o*-Toluenesulphonamide.

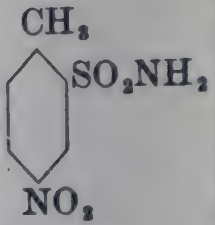


Proceed as indicated under " Preparation of dimethyl derivatives " (page 257). The dimethyl derivative will be obtained as an oil which will not solidify on cooling and shaking. Extract the oil from the mixture with 10 c.c. ether (see page 21), and wash the ethereal soln. three times with about 3 c.c. water. Separate as much water as possible, distil off the ether, cool the residual oil and stir it with a glass rod. If solidification occurs, dry the solid and determine the m.p.[4] M.p. 47° indicates that O.S. is benzenesulphonamide. The oil obtained from *o*-toluenesulphonamide does not solidify.

162° *m*-Nitrobenzenesulphonamide.

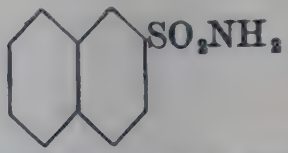


186° *p*-Nitrotoluene-2-sulphonamide.



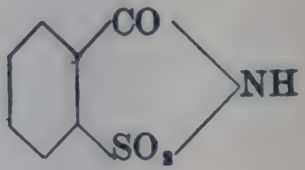
Apply Test 8*B* (page 171), when a positive result will be obtained, indicating the presence of a nitro group.

212° Naphthalene-2-sulphonamide.



Dimethyl derivative, m.p. 94° (see page 257).

222° Saccharin. (*o*-Sulphobenzimide.)



Aq. soln acid.

(*a*) In a dry t.t. place R.G. of O.S. and twice the bulk of resorcinol. Add 5 drops conc. $H_2SO_4$, and heat over a small flame until the mixture becomes dark green. Cool, dilute carefully with water to 2 c.c., then add aq. NaOH until the mixture is alkaline. Fill up the t.t. with water,
—green fluorescence.

(*b*) In a dry t.t. place 2 R.G. of O.S. and three times the bulk of solid KOH. Heat over a small flame until the solid has melted and continue heating gently for ½ min. Cool, and dissolve the solid in sufficient dil. HCl to yield an acid soln. Cool, dilute with water to 10 c.c. and add one drop aq. $FeCl_3$,
—violet colour (due to the presence of salicylic acid formed from the saccharin).

*Preparation of dimethyl derivatives of sulphonamides.*

In a 100-c.c. wide-mouthed flask place 1 g. of O.S. and add 10 c.c. aq. NaOH. Heat until soln. is complete, then add to the warm soln. 2 c.c. of dimethylsulphate (see caution, page 161). Cork the flask and shake, more or less continuously, for 5 min. Add another 10 c.c. of aq. NaOH, and boil under a reflux condenser for 5 min., in order to destroy the excess of dimethylsulphate. (The dimethyl derivative will be present as an oil.) Cool and shake well. If the oil solidifies, filter, wash the solid with cold water, crystallise from aqueous alcohol, dry, and determine the m.p.

## *SULPHONYL DERIVATIVES OF PRIMARY AND SECONDARY AMINES*

These compounds will have been indicated by Test 4 (page 250). (Only m.p.s of *p*-toluenesulphonyl derivatives of the commoner aromatic primary and secondary amines are here given.)

The identity of O.S. may be confirmed by preparing from the amine the sulphonyl derivative suspected (see page 218) and carrying out a mixed m.p. determination (see page 14).

p-*Toluenesulphonyl derivatives of aromatic primary amines.*

| M.p. | | |
|---|---|---|
| 103° | *p*-Toluenesulphonanilide | Soluble in aq. NaOH. |
| 108° | *p*-Toluenesulphon-*o*-toluidide | |
| 114° | *p*-Toluenesulphon-*m*-toluidide | |
| 117° | *p*-Toluenesulphon-*p*-toluidide | |

p-*Toluenesulphonyl derivatives of aromatic secondary amines.*

| M.p. | | |
|---|---|---|
| 87° | Ethyl *p*-toluenesulphonanilide | Insoluble in aq. NaOH. |
| 94° | Methyl *p*-toluenesulphonanilide | |

# *MISCELLANEOUS COMPOUNDS*

### *N, S, and Cl*<br>*N, S, Cl, and Na* } *present.*

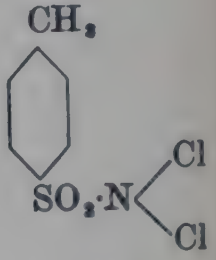
Apply the following general test for chloramines :—

To 2 c.c. of KI soln. add R.G. of O.S. and shake,—yellow or brown colour, due to liberated iodine.

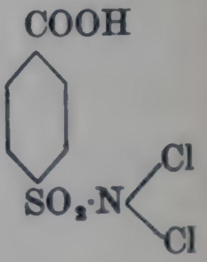
If a positive result is obtained follow the appropriate procedure, i.e. according to whether Na is absent or present.

**Sodium absent.** O.S. may be one of the following :—

Dichloramine T. (*p*-Toluenesulphondichloramide.)



Halazone. (*p*-Dichlorosulphonamidobenzoic acid.)



*Distinguishing test.*

To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 3 c.c. aq. $Na_2CO_3$, close the mouth of the t.t. and shake vigorously for 15 sec. Halazone dissolves completely, dichloramine T only slightly.

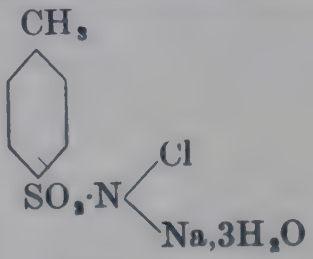
*M.p.s of chloramines, as usually encountered.*

Dichloramine T. 70°–80° (m.p. of pure compound 83°).

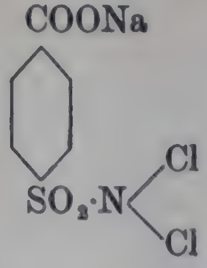
Halazone. 200°–205° with decomposition (m.p. of pure compound 213°).

**Sodium present.** O.S. may be one of the following :—

Chloramine T. (*p*-Toluene-sodium-sulphonchloramide.)



Na salt of halazone.



*Distinguishing test.*

To ¼-in. layer of O.S. in a t.t. add 10 c.c. water, heat until solution is complete, then cool. Acidify with conc. HCl, cool and shake. Filter, wash the solid well with cold water and dry. In a dry t.t. place sufficient of the dried ppt. to form a layer about ⅛-in. deep, and hold the end of the t.t. in boiling water for ½ min. The ppt. from chloramine T melts completely (the m.p. is very indefinite); that from sodium halazone does not melt (m.p. 200°–205° with decomposition).

### *P present.*

**Aryl esters of phosphoric acid.** (Phenyl and cresyl phosphates.)

*Procedure for the identification of O.S.:—*

In a 100-c.c. flask place 1 g., or 1 c.c., of O.S., 5 g. solid KOH and 10 c.c. water. Heat to boiling and continue boiling until all the oil has disappeared and any solid formed has gone into solution. (5–10 min. boiling will usually be necessary.) Allow to cool somewhat, add 30 c.c. hot water, shake round and cool. To 2 c.c. of the soln. add dil. HCl until acid, and note the carbolic odour. To this acidified soln. (filtered if an emulsion were present) add 5 c.c. ammonium molybdate soln. and allow to stand for a minute or two, when a yellow ppt. will be obtained, owing to the presence of a phosphate.

*Identification of the aryl radical.*

If O.S. is

(*a*) a solid, add 2 c.c. benzoyl chloride to the remainder of the alkaline soln. and proceed as indicated under " Benzoates " (page 52).

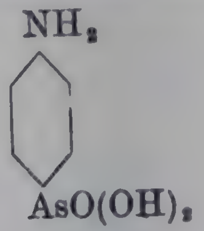
M.p. of benzoate 68° indicates that O.S. is a phenyl ester.

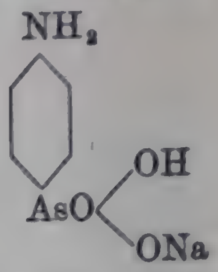
M.p. of O.S. 48° indicates that O.S. is triphenyl phosphate $(C_6H_5)_3PO_4$.

(*b*) a liquid, it will probably be tri-*o*-cresyl phosphate $(CH_3{\cdot}C_6H_4)_3PO_4$. A suitable derivative for the identification of the *o*-cresyl radical in the pure compound would be the *p*-toluenesulphonate, m.p. 53° (see page 52). As, however, only the commercial product will usually be encountered, the preparation of a derivative will be useless, since isomers of tri-*o*-cresyl phosphate will also be present.

***As, and N***
***As, N, and Na*** } ***present.***

*p*-Aminophenylarsinic acid (Arsanilic acid), and its Na salt (Atoxyl).

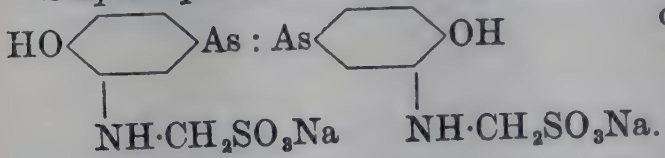




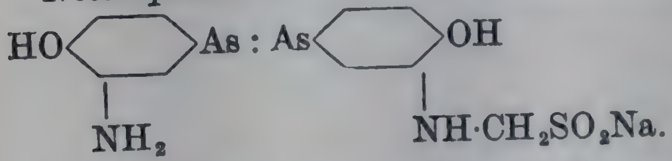
Dissolve R.G. of O.S. in 2 c.c. warm dil. HCl; cool, and add 2 c.c. of $2\frac{1}{2}\%$ aq. $NaNO_2$. Add the mixture to alkaline β-naphthol, ($\frac{1}{8}$-in. layer of β-naphthol in a t.t. dissolved in 5 c.c. aq. NaOH),—deep red colour (due to a soluble azo compound) indicating $—NH_2$ directly attached to an aromatic nucleus.

***As, N, S, Na present.***

*Sulpharsphenamine.* (Sulpharsenobenzene. Disodium 3 : 3′-diamino-4 : 4′-dihydroxyarseno-benzene-N : N′-dimethylene-bisulphite.)



*Neoarsphenamine.* (Novarsenobenzene. Sodium 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene-N-methylene-sulphoxylate.)



*Tests.* (Both substances are yellow powders, soluble in water.)

(1) To 2 c.c. dil. HCl add R.G. of O.S., boil for $\frac{1}{2}$ min., cool, and add 2 c.c. of $2\frac{1}{2}\%$ aq. $NaNO_2$. Add the mixture to alkaline β-naphthol ($\frac{1}{8}$-in. layer of β-naphthol in a t.t. dissolved in 5 c.c. aq. NaOH).
—deep red colour develops (due to the formation of a soluble azo compound).

(2) Dissolve R.G. of O.S. in 10 c.c. cold water and add 2 c.c. aq. $FeCl_3$,
—violet, or violet-red colour, indicating the presence of a phenolic group.

(3) To $\frac{1}{8}$-in. layer of O.S. in a t.t. add 1 c.c. water, warm until solution is complete, cool, and add 1 c.c. dil. HCl.

A yellow ppt. is obtained with neoarsphenamine, but not with sulpharsphenamine.

Heat the contents of the t.t. to boiling,
—evolution of $SO_2$.

# MIXTURES OF ORGANIC COMPOUNDS

*Treatment of mixtures of two or more of the following :—a nitrogenous base, an acidic substance, neutral compounds.*

Each constituent must be isolated and purified, and then identified in the manner described for single substances on page 3.

A few of the simpler methods of separation are described below, *it being assumed that not more than one substance will be removed from the mixture by any one of the particular treatments, and that any final residue after the treatments indicated will consist of only one substance.*

For details concerning extraction with ether, washing of an ethereal soln. and removal of the ether by distillation, see page 21.

Also see notes (page 263).

*Procedure :—*

Apply to the mixture the alkali-zinc test for N ; if this element is absent no base can be present, and therefore the treatment of the ethereal soln. with dil. HCl (described on page 262) should be omitted. If the mixture is a liquid follow the procedure given below ; if a solid, proceed as indicated under "Mixture solid" (page 262). The procedure should be suitably modified if it is known that the mixture contains only two constituents.

***Mixture liquid.***

Pour 10 c.c. of the mixture into a 100-c.c. wide-mouthed flask, connect the latter to a water condenser and use a dry t.t. as the receiver. Heat the contents of the flask by means of a boiling water bath. If one constituent of the mixture distils over, proceed to identify it. If the contents of the flask after cooling are (*a*) solid, proceed as indicated under "Mixture solid" (page 262), (*b*) liquid, whether any separation has been effected or not, add 30 c.c. *dry* ether. Shake round, and pour the contents of the flask into a 100-c.c. separating funnel (preferably pear-shaped). Insert the stopper, shake well, and allow to stand for a minute or two.

If (i) the liquid has dissolved completely in the ether, proceed as indicated under "Mixture solid" (*b*).

(ii) a lower layer of liquid is present, run it off into a small separating funnel, add 10 c.c. *dry* ether (in order to remove any of the other constituents of the mixture), shake and allow to settle. Run off the lower layer into a dry t.t. and identify it (probably a polyhydric alcohol). Pour the ether from the small funnel into the larger one, and proceed as indicated under " Mixture solid " (*b*).

***Mixture solid.***

Introduce about 5 g. of the finely powdered solid into a 100-c.c. separating funnel, add 30 c.c. *dry* ether and shake well.

If (*a*) some solid remains undissolved, shake round and pour the contents of the funnel through the neck into a filter.

Transfer any solid remaining in the funnel to the filter by washing it out with small quantities of dry ether.

Finally wash the solid in the filter with dry ether, in order to remove the other constituents of the mixture, and allow the washings to fall into the main filtrate. Pour the filtrate into the separating funnel, and proceed as indicated under (*b*). Identify the solid substance, which may be one of the following :—a metallic salt, a carbohydrate, a polyhydric alcohol, a salt of an organic base with a mineral acid, a sulphonic acid, an amide.

(*b*) the solid has dissolved completely in the ether, proceed as follows :—

To the ethereal soln. in the funnel add 30 c.c. dil. HCl, insert the stopper, shake well, and allow to stand until two well-defined layers are formed. Run off the lower layer (HCl extract) into a beaker.

*Treatment of the HCl extract*, which may contain the hydrochloride of a base (only aromatic bases which are insoluble or sparingly soluble in water are here considered) :—

Add 20% aq. KOH with stirring until the soln. is alkaline. Cool and stir ; if no solid separates scrape the glass in contact with the liquid with a glass rod.

If a base separates as

(i) a solid, filter it off, wash it well with cold water, dry, and identify it.

(ii) an oil or emulsion, pour the contents of the beaker into a separating funnel and add 10–15 c.c. ether.

Shake, separate and reject the lower layer.

Wash the ethereal soln. with distilled water until the wash-water, after running off, gives not more than a slight turbidity on the addition of dil. $HNO_3$ and aq. $AgNO_3$.

Distil off the ether and identify the residual base.

*Treatment of the main ethereal soln.* (after extraction with dil. HCl) :—

If a base has been isolated from the HCl extract, add to the ethereal soln. 10 c.c. dil. HCl, shake, run off and reject the lower layer. (This is to remove any remaining basic constituent from the ethereal soln., and, of course, will not be necessary if no base has been isolated.)

Add to the ethereal soln. 30 c.c. of aq. NaOH, shake well, and run off the lower layer (NaOH extract) into a beaker.

*Treatment of the NaOH extract*, which may contain the sodium derivative of one of the following: a carboxylic acid, a phenolic compound, a $\beta$-ketonic ester, a sulphonamide, saccharin, a sulphonyl derivative of a primary amine, a member of the purine group :—

Just acidify with conc. HCl, cool and stir; if no solid separates scrape the glass in contact with the liquid with a glass rod.

If (*a*) a solid separates, filter it off, wash it well with cold water, dry, and identify it.

(*b*) no solid separates, pour the contents of the beaker into a separating funnel and extract with 10–15 c.c. ether. (If the acidification produced an oil or emulsion one extraction will be sufficient; if, however, no oil or emulsion was obtained at least three extractions should be carried out and the several ethereal extracts added together. This is necessary since a water-soluble compound may have been liberated by the HCl.)

Wash the ethereal extract several times with 3 c.c. distilled water until the wash-water, after separation, gives not more than a slight turbidity on the addition of dil. $HNO_3$ and aq. $AgNO_3$. Distil off the ether and identify any residue.

*Treatment of the main ethereal soln.* (after extraction with aq. NaOH) which may contain one of the following neutral compounds: a hydrocarbon, an alcohol, an ester, an ether, an aldehyde, a ketone. a nitrile, etc. (substituents such as $NO_2$ or halogen may be present in these compounds) :—

Wash the ethereal soln. with distilled water until the wash-water is no longer alkaline. Distil off the ether and identify any residue

NOTES.

(1) Owing to the fact that ether is somewhat soluble in water, it may be necessary to add more of the former from time to time. Indications of the necessity for more ether are

(*a*) the ethereal soln. becoming cloudy.

(*b*) an imperfect separation of the ethereal and aqueous layers.

(2) If a solid is produced on the addition to the ethereal soln. of dil. HCl, or of aq. NaOH, filter by suction the whole contents of the separating funnel. Wash the solid well with ether, allowing the washings to fall into the first filtrate. Wash out the separating funnel with water, pour the filtrate into it and run off the lower layer. Treat the solid, or the solid and the

lower layer, in the appropriate manner, described either under "Treatment of the HCl extract," or under "Treatment of the NaOH extract." (The presence of a solid will be due to the formation of a sparingly soluble sodium salt, such as sodium cinnamate, or to the formation of a sparingly soluble hydrochloride, such as that of benzylaniline.)

(3) The scheme of separation may be extended as follows :—

(*a*) The NaOH extract, before acidifying with conc. HCl, might be saturated with $CO_2$, when a weakly acidic substance (e.g. a phenolic compound with no $NO_2$ groups), if present as alkali salt, would be liberated and could be isolated by filtration or by extraction with ether.

The procedure is similar to that described under "No alcohol has been detected" (page 104).

(*b*) The ethereal soln. after the various treatments might be shaken with a saturated soln. of sodium bisulphite.

An aldehyde, and in some cases a ketone, if present would thus be converted into its bisulphite compound, the latter being present either as a solid (for procedure see note 2), or in solution in the lower layer.

On heating the solid or lower layer with HCl or $Na_2CO_3$ the aldehyde or ketone would be regenerated, and could be isolated by filtration or by extraction with ether.

Since the commercial product may be unsatisfactory, the bisulphite soln. should be prepared as follows :—

Into a mixture of 200 g. $NaHCO_3$ and 450 c.c. water pass $SO_2$ until all the solid has dissolved and the solution is just acid to methyl orange.

# SPECIAL REAGENTS

## Alkali-sugar and alkali-zinc mixtures.

### *Alkali-sugar mixture.*

An intimate mixture of pure anhydrous sodium carbonate and one-tenth of its weight of pure sucrose.

When organic compounds are heated with this mixture, halogens are converted into sodium halides, sulphur into sodium sulphide, and nitrogen (in a limited number of cases) into sodium cyanide.

The proportion of sugar employed does not cause excessive fumes when the mixture is heated, yet provides sufficient carbon for the reduction of sulphate, etc., to sulphide. The final heating to redness is essential, in order to cause any such reduction, to decompose the sugar thoroughly, and to remove any deposit from the mouth of the tube, so that a perfectly colourless filtrate is obtained.

### *Alkali-zinc mixture.*

An intimate mixture of zinc dust and half its weight of anhydrous sodium carbonate (ordinary commercial products).

The gradual heating of the organic substance is necessary, as otherwise negative results in the test for nitrogen may be obtained with aromatic bases and their salts and derivatives.

The alkali-zinc mixture, with constituents of A.R. quality, may also be used to test for sulphur and halogens, provided that the tests for chlorine and sulphur are made in comparison with a blank test. (Middleton.)

The test for sulphur is carried out as follows :—After the hot tube has been plunged into water, the mixture is heated to boiling and allowed to settle, and the liquid is then decanted through a filter. To the residue in the dish (containing insoluble zinc sulphide if sulphur is present in the organic compound) are added about 10 c.c. of dilute hydrochloric acid, and a filter paper (upon the centre of which a drop of sodium plumbite solution has been poured) is immediately placed over the dish. If sulphur is present in the organic compound, a dark brown stain, visible on the upper surface of the paper, will be formed.

Blank tests usually give a slight brown stain visible only on the under surface of the paper.

*Advantages of the alkali-sugar and alkali-zinc mixtures.*

(i) The mixtures are readily prepared (it is not necessary to dry the sodium carbonate) and convenient to handle, and may be kept without any special precautions.

(ii) The tests are applicable without modification to very volatile substances, e.g. ethyl bromide (b.p. 38°).

(iii) Except in the case of picric acid and picrates of organic compounds the reactions are perfectly quiet, even with nitrates and polynitro compounds.

With picric acid and picrates, the mixture, or a portion of it, is harmlessly ejected from the tube, this behaviour affording an indication of this class of compound.

(iv) The plunging of the hot tube into water is attended with less danger than when an alkali metal is used.

(v) No cyanide is formed when either mixture is heated alone.

When a mixture of one part of magnesium powder to two parts of potassium carbonate (Castellana) is strongly heated alone, under the conditions essential for carrying out the test with a very volatile substance, i.e. in an ignition tube, sufficient cyanide is formed to give a dense blue precipitate when the nitrogen test is applied.

(vi) The alkali-zinc test has the great advantage over all other methods, that the test for nitrogen is not interfered with by the presence of sulphur in the organic compound, no sulphide or thiocyanate being present in the alkaline filtrate containing the cyanide.

### Alkaloidal reagents.

See page 244.

### Barfoed's reagent.

Dissolve 13 g. of crystallised neutral copper acetate in 200 c.c. of cold 1% acetic acid soln.

### Bromine in carbon tetrachloride.

Dissolve 4 c.c. bromine in 100 c.c. carbon tetrachloride.

### Bromine water.

Shake 5 c.c. bromine with 100 c.c. water until no more of the bromine will dissolve. Allow the excess of bromine to remain in the solution.

### Chlorine water.

Pass chlorine into cold water until a saturated solution is obtained.

### Denigès solution.

Dissolve, by warming, 5 g. of yellow mercuric oxide in a mixture of 20 c.c. conc. $H_2SO_4$ and 100 c.c. water. Cool and filter.

### Dichromate mixture.

Dissolve 100 g. of sodium dichromate in a mixture of 250 c.c. conc. $H_2SO_4$ and 750 c.c. water.

### 3 : 5-Dinitrobenzoyl chloride.

This reagent is employed for the conversion of alcohols and phenols into solid esters. Since the reagent decomposes on keeping under ordinary conditions, it is advisable to prepare it as required by the action of $PCl_5$ on 3 : 5-dinitrobenzoic acid.

*Preparation of 3 : 5-dinitrobenzoates of alcohols.*

In a porcelain dish place 0·3 g. of 3 : 5-dinitrobenzoic acid and add ¼-in. layer in a t.t. of powdered $PCl_5$. Grind the substances together with a pestle until the mixture becomes semi-solid. Add 1 c.c. of the alcohol and stir round. Allow to stand, with periodic stirring, for 5 min. if the alcohol is primary, or for 30 min. if the alcohol is secondary (tertiary alcohols do not form an ester under these conditions). Add 20 c.c. of approx. 2N. $Na_2CO_3$ and stir for a minute or so, then filter off the solid. Wash the solid with cold water, crystallise it from a mixture of 2 pts. of alcohol and 1 pt. of water (see note), dry, and determine the m.p.

NOTE.

In some cases it may be necessary to add more alcohol in order to effect solution of the derivative. Derivatives of low m.p. such as *n*-amyl 3 : 5-dinitrobenzoate, m.p. 46°, should be dissolved in petroleum ether and air blown, by means of bellows, over the surface of the liquid until the derivative crystallises out.

| | | | |
|---|---|---|---|
| Methyl | 3 : 5-dinitrobenzoate | m.p. | 107° |
| Ethyl | ,, ,, | ,, | 93° |
| *n*-Propyl | ,, ,, | ,, | 73° |
| *iso*-Propyl | ,, ,, | ,, | 122° |
| *n*-Butyl | ,, ,, | ,, | 64° |
| *iso*-Butyl | ,, ,, | ,, | 87° |
| *sec*-Butyl | ,, ,, | ,, | 76° |
| *n*-Amyl | ,, ,, | ,, | 46° |
| *cyclo*-Hexanol | ,, ,, | ,, | 112° |

### Fehling's solution.

(1) Dissolve 69·3 g. of pure crystallised copper sulphate in water containing a few drops of dil. $H_2SO_4$ and make up to 1 litre.
(2) Dissolve 346 g. of Rochelle salt (sodium potassium tartrate) and 120 g. of NaOH in water and make up to 1 litre.

For qualitative work mix approximately equal volumes immediately before use.

**Schiff's reagent.**

Dissolve 1 g. of a rosaniline salt in 100 c.c. warm water. Pass $SO_2$ until no further change occurs. Filter, and keep the filtrate as a stock solution.

Dilute 10 c.c. of the stock solution with water to 1 litre, add 50 c.c. of a saturated aqueous soln. of $SO_2$ and allow to stand overnight.

**Sodium nitrite solution (2½%).**

Dissolve 12·5 g. of $NaNO_2$ in 500 c.c. water.

**Sodium nitroprusside solution (½%).**

Dissolve 0·1 g. in 20 c.c. water. The solution deteriorates on keeping, becoming green.

**Common reagents.**

Acids (dilute) and alkalies (aqueous).

Approx. 2N.

Alcohol.

Industrial spirit unless absolute alcohol is specified.

Ferric chloride (freshly prepared).

5 g. of hydrated salt dissolved in water and made up to 100 c.c.

Other reagents as used for Inorganic Analysis.

# INDEX OF ORGANIC PROCESSES AND PREPARATIONS

## WITH SUGGESTED EXERCISES FOR STUDENTS WHO DO NOT REQUIRE IDENTIFICATION WORK

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